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CHEMICAL PROCESS PRINCIPLES

Part Three

KINETICS AND CATALYSIS

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PREFACE

"In the following pages certain industrially important principles of chemistry and physics have been selected for detailed study. The significance of each principle is intensively developed and its applicability and limitations scrutinized." Thus reads the preface to the first edition of *Industrial Chemical Calculations*, the precursor of this book. The present book continues to give intensive quantitative training in the practical applications of the principles of physical chemistry to the solution of complicated industrial problems and in methods of predicting missing physicochemical data from generalized principles. In addition, through recent developments in thermodynamics and kinetics, these principles have been integrated into procedures for process design and analysis with the objective of arriving at optimum economic results from a minimum of pilot-plant or test data. The title *Chemical Process Principles* has been selected to emphasize the importance of this approach to process design and operation.

The design of a chemical process involves three types of problems, which although closely interrelated depend on quite different technical principles. The first group of problems is encountered in the preparation of the material and energy balances of the process and the establishment of the duties to be performed by the various items of equipment. The second type of problem is the determination of the process specifications of the equipment necessary to perform these duties. Under the third classification are the problems of equipment and materials selection, mechanical design, and the integration of the various units into a coordinated plot plan.

These three types may be designated as process, unit-operation, and plant-design problems, respectively. In the design of a plant these problems cannot be segregated and each treated individually without consideration of the others. However, in spite of this interdependence in application the three types may advantageously be segregated for study and development because of the different principles involved. Process problems are primarily chemical and physicochemical in nature; unit-operation problems are for the most part physical; the plant-design problems are to a large extent mechanical.

In this book only process problems of a chemical and physicochemical nature are treated, and it has been attempted to avoid overlapping into the fields of unit operations and plant design. The first part deals primarily with the applications of general physical chemistry, thermophysics, thermochemistry, and the first law of thermodynamics. Generalized procedures for estimating vapor pressures, critical constants, and heats of vaporization have been elaborated. New methods are presented for dealing with equilibrium problems in extraction, adsorption, dissolution, and crystallization. The construction and use of enthalpy-concentration charts have been extended to complex systems. The treatment of material balances has been elaborated to include the effects of recycling, by-passing, changes of inventory, and accumulation of inerts.

In the second part the fundamental principles of thermodynamics are presented with particular attention to generalized methods. The applications of these principles to problems in the compression and expansion of fluids, power generation, and refrigeration are discussed. However, it is not attempted to treat the mechanical or equipment problems of such operations.

Considerable attention is devoted to the thermodynamics of solutions with particular emphasis on generalized methods for dealing with deviations from ideal behavior. These principles are applied to the calculation of equilibrium compositions in both physical and chemical processes.

Because of the general absence of complete data for the solution of process problems a chapter is devoted to the new methods of estimating thermodynamic properties by statistical calculations. This treatment is restricted to simple methods of practical value.

All these principles are combined in the solution of the ultimate problem of the kinetics of industrial reactions. Quantitative treatment of these problems is difficult, and designs generally have been based on extensive pilot-plant operations carried out by a trial-and-error procedure on successively larger scales. However, recent developments of the theory of absolute reaction rates have led to a thermodynamic approach to kinetic problems which is of considerable value in clarifying the subject and reducing it to the point of practical applicability. These principles are developed and their application discussed for homogeneous, heterogeneous, and catalytic systems. Particular attention is given to the interpretation of pilot-plant data. Economic considerations are emphasized and problems are included in establishing optimum conditions of operation.

In covering so broad a range of subjects, widely varying comprehensibility is encountered. It has been attempted to arrange the material in the order of progressive difficulty. Where the book is used for college instruction in chemical engineering the material of the first part is suitable for second- and third-year undergraduate work. A portion of the second part is suitable for third- or fourth-year undergraduate work; the remainder is of graduate level.

The authors wish to acknowledge gratefully the assistance of Professor R. A. Ragatz in the revision of Chapters I and VI, and the suggestions of Professors Joseph Hirschfelder, R. J. Altpeter, K. A. Kobe, and Dr. Paul Bender.

Olaf A. Hougen
Kenneth M. Watson

Madison, Wisconsin
August, 1943

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CHEMICAL PROCESS PRINCIPLES CHARTS. *Second Edition*

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CHEMICAL PROCESS PRINCIPLES
Part 1—Material and Energy Balances. *Second Edition*
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Part 3—Kinetics and Catalysis

TABLE OF SYMBOLS

A	area
A	atomic weight
A	component A
A	total work function
a	activity
a_m	external surface per unit mass
a_p	external surface per particle
a_v	external surface per unit volume
B	component B
B	constant of Calingaert–Davis equation
B	thickness of effective film
C	component C
C	concentration per unit volume
C	degrees centigrade
C	number of components
C	over-all rate constant
C_p	heat capacity at constant pressure
C_v	heat capacity at constant volume
C_s	Sutherland constant
c	concentration of adsorbed molecules per unit mass of catalyst
c	specific heat
c	velocity of light
c_p	molal heat capacity at constant pressure
c_v	molal heat capacity at constant volume
c'	surface concentration of adsorbed molecules per unit catalyst area
D	diameter
D_{AB}	diffusivity of A and B
D_p	effective particle diameter equal to diameter of sphere having the same external surface area as particle
D'_p	effective diameter equal to diameter of sphere having same area per unit volume as particle
d	differential operator
E	energy in general
E	energy of activation, Arrhenius equation
E_A	effectiveness factor of catalysis

e	base of natural logarithms
F	degrees of freedom
F	feed rate
F	force
F_e	external void fraction
F_i	internal void fraction
f	friction factor
f	fugacity
f	weight fraction
G	free energy
G	mass velocity per unit area
G	specific gravity
G	free energy per mole
$\overline{\mathrm{G}}$	partial molal free energy
ΔG	change in free energy
(g)	gaseous state
g	degeneracy
g_c	standard gravitational constant, 32.174 (ft/sec)/sec
H	enthalpy
H	Henry's constant
H	humidity
H_c	height of catalytic unit
H_d	height of mass-transfer unit
H_h	height of heat-transfer unit
H_p	height equivalent to a theoretical plate
H_p	percentage humidity
H_R	height of reactor unit
H_r	relative humidity
H_t	height of transfer unit
ΔH	change in enthalpy
ΔH_c	heat of combustion
ΔH_f	heat of formation
ΔH_r	heat of reaction
$\Delta H^{\ddagger}$	standard enthalpy of activation
H	enthalpy per mole
$\overline{\mathrm{H}}$	partial molal enthalpy
$\Delta\overline{\mathrm{H}}$	partial molal enthalpy change
h	Planck's constant
h	heat-transmission coefficient
I	inert component
I	integration constant
I	moment of inertia

J	Jacobian function
J	mechanical equivalent of heat
j_d	mass-transfer factor in fluid film
j_h	heat-transfer factor in fluid film
K	characterization factor
K	degrees Kelvin
K	distribution coefficient
K	equilibrium constant
K	vaporization equilibrium constant
K_a	equilibrium constant for adsorption
K_c	equilibrium constant, concentration units
K_g	over-all mass-transfer coefficient, pressure units
K_L	over-all mass-transfer coefficient, liquid concentration units
K_p	equilibrium constant, pressure units
K'	surface equilibrium constant
k	forward-reaction velocity constant
k	thermal conductivity
$\boldsymbol{k}$	Boltzmann constant
k_A	adsorption velocity constant
k'_A	desorption velocity constant
k_G	mass-transfer coefficient, gas film
k_L	mass-transfer coefficient, liquid film
k'	reverse-reaction velocity constant
L	mass velocity of liquid per unit area
L	total molal adsorption sites per unit mass
L_M	molal mass velocity of liquid per unit area
L'	active centers per unit area of catalyst
l	length
l_p	heat of pressure change at constant pressure
l_v	heat of expansion at constant temperature
(l)	liquid state
ln	natural logarithm
log	logarithm to base 10
M	molecular weight
M_m	mean molecular weight
m	mass
m	slope of equilibrium curve dy^*/dx
m	Thiele modulus
N	Avogadro number $6.023(10^{23})$
N	mole fraction
N_t	number of transfer units

N_G	number of transfer units, gas film
N_L	number of transfer units, liquid film
n	number of moles
P	pressure (used only in exceptional cases to distinguish pressure of pure components from partial pressures of some component in solution)
p_f	factor for unequal molal diffusion in gas film
Q	heating value of fuel
Q	partition function
q	heat *added to* a system
q_r	rate of heat flow
R	component R
R	gas constant
r	radius
r_{aA}	rate of reaction or transfer of A per unit area
r_{mA}	rate of reaction or transfer of A per unit mass
r_{vA}	rate of reaction or transfer of A per unit volume
S	component S
S	cross section
S	entropy
S	humid heat
S_p	percentage saturation
S_r	relative saturation
S_v	space velocity
$\Delta S^\ddagger$	entropy of activation
s	molal entropy
s	number of equidistant active sites adjacent to each other
(s)	solid state
T	absolute temperature, degrees Rankine or Kelvin
t	temperature, °F or °C
U	internal energy
U	over-all heat-transfer coefficient
U	internal energy per mole
u	velocity
V	molecular volume in Gilliland equation
V	volume
V_r	volume of reactor
v	volume per mole
w	weight
w	work *done by* system
w_e	work of expansion *done by* system

w_f	electrical work *done by* system
w_s	shaft work
$X^\ddagger$	activated complex
x	mole fraction in liquid phase
x	mole fraction of reactant converted in feed
x	quality
y	mole fraction in vapor
y^*	mole fraction in vapor, equilibrium value
Z	elevation above datum plane
Z	height or thickness of reactor
z	compressibility factor
z	mole fraction in total system

DIMENSIONLESS NUMBERS

N_{Re}	Reynold's number	$\frac{DG}{\mu}$
N_{Pr}	Prandtl number	$\frac{C_p\mu}{k}$
N_{St}	Stanton number	$\frac{h}{C_pG}$
N_{Sc}	Schmidt number	$\frac{\mu}{\rho D_v}$

SUBSCRIPTS

A	component A
a	air
B	component B
b	normal boiling point
C	component C
c	critical state
D	component D
D	dense arrangement
e	expansion
f	electrical and radiant
f	formation
f	fusion
G	gas or vapor
H	isenthalpic
L	liquid
L	loose arrangement

p	constant pressure
R	component R
r	reduced conditions
r	relative
S	component S
S	isentropic
s	normal boiling point
s	saturation
T	isothermal
t	temperature
t	transition
V	constant volume
v	vapor
w	water vapor

GREEK SYMBOLS

(α)	crystal form
α	coefficient of compressibility
α	proportionality factor for diffusion
α	relative volatility
α	thermal diffusivity
(β)	crystal form
β	coefficient of volumetric expansion
γ	activity coefficient
(γ)	crystal form
Δ	finite change of a property; positive value indicates an increase
δ	change in moles per mole of reactant
δ	deformation vibration
∂	partial differential operator
ϵ	energy per molecule
η	efficiency
θ	fraction of total sites covered
κ	ratio of heat capacities
Λ	heat of vaporization
λ	heat of vaporization per mole
λ	wave length
λ_f	heat of fusion per mole
μ	chemical potential
μ	viscosity
ν	frequency
ν	fugacity coefficient of gas

ν	number of ions
ν	number of molecules
ν	valence or stretching vibration
ω	expansion factor of liquid
ω	wave number
π	total pressure of mixture, used where necessary to distinguish from p
ρ	density
ρ_B	bulk density
ρ_P	particle density
ρ_C	true solid density
Σ	summation
σ	surface tension
σ	symmetry number
τ	time
ϕ	activity coefficient
ϕ	number of phases

SUPERSCRIPTS

$*$	ideal behavior
$*$	equilibrium state
$^\circ$	standard state
$'$	pseudo state
$'$	reverse rate
$\ddagger$	standard state of activation

CHAPTER XVIII

HOMOGENEOUS REACTIONS

The economy of chemical manufacture depends largely upon establishing high rates of production of desired products and minimizing the production of undesired by-products. Thermodynamic principles may permit selection of conditions which will result in favorable production if equilibrium is reached but give no clue as to the rates at which the various reactions occur. Thus, the displacement of a system from equilibrium conditions may be considered as a potential which may cause a reaction to proceed if other conditions are favorable. This displacement is analogous to an electric voltage which may cause a flow of electricity. However, the rate of current flow is dependent on the conductance of the system as well as on the voltage. Similarly, reaction rates depend on the kinetic properties of the system as well as on the driving potential. Quantitative knowledge of these kinetic properties is desirable in the design and intelligent operation of a chemical process.

Industrial processes rarely reach equilibrium and in general are desired to proceed toward only a partial equilibrium among the many reactions possible in a complex system. In many cases if complete equilibrium were reached undesirable by-products would predominate. However, by proper selection of conditions the rate of formation of such by-products may be suppressed and good yields of the desired product obtained at conditions far removed from complete equilibrium. It is thus evident that the kinetic properties of a system may determine not only the size and capacity of process equipment but the yields and qualities of the products as well. All three factors are of vital economic significance.

Classification of Reactions. Chemical reactions may be classified as *homogeneous* if only one phase is involved or *heterogeneous* if more than one phase actively participates in the reaction. Where catalytic surfaces are present, a reaction may proceed simultaneously by a homogeneous mechanism in the main body of the fluid and by a heterogeneous mechanism at the catalytic surfaces. In many cases even the walls of a reactor exert catalytic effects to such an extent that the rates of presumably homogeneous reactions are found to vary with the ratio of surface to volume.

A further classification is as *flow* and *nonflow* or *batch* processes. Both types are of industrial importance, and it is frequently necessary to interpret data obtained in the laboratory under nonflow conditions to serve as a basis for the design of a commercial process under flow conditions.

On the basis of the conditions of restraint a reaction may be classified as isothermal, adiabatic, constant pressure, or constant volume. All four types are of industrial importance, and the general case of a nonadiabatic process occurring under simultaneously varying conditions of temperature and pressure is frequently encountered.

Order of Reaction. For the general reaction $aA + bB + cC \cdots \leftrightarrows rR + sS \cdots$ which results from the *simultaneous* combination of a molecules of A, b molecules of B, and c molecules of $C \cdots$ the reaction rate for the forward reaction may be written as

$$r_u = ka_A^a a_B^b a_C^c \cdots \tag{1}$$

Similarly, for the reverse reaction,

$$r'_u = k' a_R^r a_S^s \cdots \tag{2}$$

where

r_u, r'_u = unidirectional rates of reaction in moles of a particular compound formed or consumed per unit volume of reacting system per unit time

k, k' = the reaction velocity constants

a_A, $a_B \cdots$ = activities of components A and B, etc.

The net rate of the reaction as written is then

$$r = r_u - r'_u = ka_A^a a_B^b a_C^c \cdots - k' a_R^r a_S^s \cdots \tag{3}$$

At equilibrium, where $r = 0$,

$$\frac{a_R^r a_S^s \cdots}{a_A^a a_B^b a_C^c \cdots} = \frac{k}{k'} = K \tag{4}$$

where K = the equilibrium constant

Combination of (3) and (4) gives

$$r = k\left(a_A^a a_B^b a_C^c \cdots - \frac{a_R^r a_S^s \cdots}{K}\right)$$

It is mathematically permissible to write any form of equation such as (1) or (2) which involves an otherwise undefined proportionality factor. The choice of the particular form of Equations (1) and (2) is justified by experimental evidence that under many ideal conditions the proportionality factors are constants which depend only on temperature and the nature of the reaction. Thus, Equations (1) and (2) serve to define the reaction velocity constants k and k' which must be recognized as inherently different from the classical reaction velocity constants of chemical kinetics. Because many of the early laboratory studies were carried out under conditions of constant volume it was convenient to define reaction rates as rates of change of concentration expressed in moles per unit volume. Since concentrations are changed by change of volume as well as by reaction, the rate of change of concentration is a proper expression for rate of reaction only in a system of constant volume. Similarly, the classical law of mass action was formulated in terms of concentrations, and kinetic equations were developed to relate rate of change of concentration to the concentrations of the reactants. As commonly written, such equations are restricted to conditions of constant volume, and the reaction velocity constants so defined have different dimensions and significance from those of Equations (1) and (2). The relationships between reaction velocity constants expressed in terms of activities and those in terms of concentrations are discussed on page 820.

The *order of the forward reaction* is equal to the sum of the exponents a, b, $c \cdots$ of Equation (1). This sum is equal to 1.0 for a first-order reaction, 2.0 for a second-order reaction, and 3.0 for a third-order reaction. In reactions of *simple order* the exponents of the activity terms in the fundamental rate equation are equal to the minimum number of reactant molecules which must simultaneously combine in order to effect the reaction. This minimum number of combining molecules is termed the *molecularity* of the reaction. For reactions of simple order the order is equal to molecularity. Thus, a simple first-order reaction is unimolecular, and a simple second-order reaction is bimolecular.

It is important to recognize that the exponents a, b, c in Equation (1) and r and s in Equation (2) correspond to the number and kind of molecules which *actually simultaneously combine and do not necessarily correspond to the molecular proportions used in the stoichiometric equation representing the over-all reaction.* For example, the synthesis of methanol from carbon monoxide and hydrogen is represented by the stoichiometric equation $CO + 2H_2 \rightarrow CH_3OH$. However, it is probable that in a homogeneous reaction the alcohol results from secondary hydrogenation of formaldehyde which is formed as a primary product. Similarly, the combustion of a gas such as benzene actually proceeds by a succession of low-order reactions and never by the mechanism suggested by stoichiometry. Thus, Equations (1) and (2) are applicable only to individual chemical steps in one direction and not to over-all stoichiometric results. In this respect kinetic equations differ from thermodynamic equilibrium relationships which are independent of the mechanism of the reaction and dependent only upon the over-all results.

In the application of Equation (1) or (2) to a single chemical step the exponents a, b, $c \cdots$ are integers whose sum is probably never greater than three.

Theory of Absolute Reaction Rates. Eyring and coworkers[1] have developed from the principles of statistical mechanics a theory which permits calculation of reaction velocity constants from a knowledge of chemical structure and energy distribution without actual rate measurements. However, in its present state of development rates calculated by this method may be in error by a factor of from 10 to 100 or more. In view of the wide variations of reaction rates this degree of agreement furnishes confirmation of the theory but is not sufficient to serve as a basis for process design. For this reason the engineering utility of the method is limited to rational extension of fragmentary rate data rather than to the prediction of rates.

According to the Eyring theory a chemical reaction is preceded by the formation from the reactant molecules of an *activated complex* which then decomposes to form the final products. The activated complex is considered as present in the reacting system in continual thermodynamic equilibrium with the reactants. Thus, if reactants A and B combine to form products R and S, the reaction is considered as proceeding in two steps as follows,

$$aA + bB \rightleftarrows X^{\ddagger} \rightarrow rR + sS \tag{5}$$

where $X^{\ddagger}$ represents the activated complex formed by A and B. Since equilibrium is maintained between the reactants and the activated complex, the rate of the reaction is determined by the rate of decomposition of the complex. If the properties of the activated complex are identified by the superscript ‡, there results

$$\frac{a^{\ddagger}}{a_A^a a_B^b} = K^{\ddagger} \tag{6}$$

where

$a^{\ddagger}$, a_A, and a_B = activities of the activated complex and reactants A and B, respectively

$K^{\ddagger}$ = the equilibrium constant between the reactants and the activated complex

By statistical mechanics it was developed by Eyring that in the majority of cases the rate of decomposition of the activated complex and, therefore, the rate of the reaction, is given by the following equation,

---

[1] S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Company, New York (1941).

$$r_u = \frac{\mathbf{k}T}{\mathbf{h}} c^{\ddagger} \tag{7}$$

where r_u = rate of decomposition, moles/(sec)(unit volume)

$c^{\ddagger}$ = concentration of activated complex, moles per unit volume = $N^{\ddagger}/v_m$

$\mathbf{k}$ = Boltzmann constant = $(1.3805)10^{-16}$ erg/(°K)(molecule)

$\mathbf{h}$ = Planck constant = $(6.6240)10^{-27}$ erg-sec per molecule

$\dfrac{\mathbf{k}}{\mathbf{h}}$ = $(2.0842)10^{10}$ per (°K)(sec)

$N^{\ddagger}$ = mole fraction of the activated complex

v_m = average molal volume of the system

In dealing with liquid systems or with gases which do not form ideal solutions, the standard state for the expression of activities is conveniently taken as that of the pure components at the temperature and pressure of the system:

$$a^{\ddagger} = \gamma^{\ddagger} N^{\ddagger} = \gamma^{\ddagger} c^{\ddagger} v_m \tag{8}$$

$\gamma^{\ddagger}$ = activity coefficient of the activated complex

Combining Equations (7) and (8), with this choice of standard states gives

$$r_u = \frac{\mathbf{k}T}{\mathbf{h}} \frac{a^{\ddagger}}{\gamma^{\ddagger} v_m} \tag{9}$$

When ideal solutions of gases are dealt with, where it is convenient to select as the standard state the pure components at the temperature of the system and a unit fugacity of 1 atm,

$$a^{\ddagger} = \nu^{\ddagger} \pi N^{\ddagger} \tag{10}$$

and

$$c^{\ddagger} = \frac{N^{\ddagger}}{v_m} = \frac{N^{\ddagger}\pi}{z_m R' T} \tag{11}$$

Combining (10) and (11) gives

$$c^{\ddagger} = \frac{a^{\ddagger}}{\nu^{\ddagger} z_m R' T} \tag{12}$$

where

$\nu^{\ddagger}$ = fugacity coefficient of the activated complex

z_m = mean compressibility factor of the mixture

π = total pressure, atmospheres

R' = gas law constant in units consistent with π, v_m, and T

Combining (7) and (12) gives

$$r_u = \frac{\mathbf{k}}{\mathbf{h}R'} \frac{a^\ddagger}{\nu^\ddagger z_m} \tag{13}$$

Expressions for the reaction velocity constant are obtained by combining Equations (1) and (6) with (9) or (13). Thus, where unit activity is equal to unit mole fraction,

$$k = \frac{\mathbf{k}T}{\mathbf{h}\gamma^\ddagger v_m} \frac{a^\ddagger}{a_A^a a_B^b} = \frac{\mathbf{k}T}{\mathbf{h}} \frac{K^\ddagger}{v_m \gamma^\ddagger} \tag{14}$$

For gaseous systems approximating ideal solutions,

$$k = \frac{\mathbf{k}}{\mathbf{h}R' z_m \nu^\ddagger} \frac{a^\ddagger}{a_A^a a_B^b} = \frac{\mathbf{k}}{\mathbf{h}R'} \frac{K^\ddagger}{z_m \nu^\ddagger} \tag{15}$$

It is evident from Equations (14) and (15) that for a given reaction the values of k and $K^\ddagger$ are dependent upon the choice of the standard state. Thus the k and $K^\ddagger$ of Equation (15) are numerically different from those of Equation (14) and must be used with care to maintain a consistent choice of standard state.

Equations (14) and (15) express the reaction velocity constant in thermodynamic terms involving $K^\ddagger$ the equilibrium constant relating the activated complex and the reactants. Thus, by evaluation of the thermodynamic properties of the activated complex and the reactants the rate of a reaction is established. Since $K^\ddagger$ is a true equilibrium constant expressing the ratio of the activities of products to reactants, it may be expressed in terms of the standard free-energy change in forming the activated complex. Thus,

$$K^\ddagger = e^{-\frac{\Delta G^\ddagger}{RT}} = e^{-\frac{\Delta H^\ddagger}{RT} + \frac{\Delta S^\ddagger}{R}} \tag{16}$$

where $\Delta G^\ddagger$, $\Delta H^\ddagger$, $\Delta S^\ddagger$ = the free energy, enthalpy, and entropy changes, respectively, accompanying the formation of the activated complex from the reactants all in their standard states. It should be noted that $K^\ddagger$ is dimensionless only for first-order reactions. Combining Equations (16) and (14), for liquid systems yields

$$k = \frac{\mathbf{k}T}{\mathbf{h}\gamma^\ddagger v_m} e^{-\frac{\Delta H^\ddagger}{RT} + \frac{\Delta S^\ddagger}{R}} \tag{17}$$

or for gases, if (15) and (16) are combined,

$$k = \frac{\mathbf{k}}{\mathbf{h}\nu^\ddagger z_m R'} e^{-\frac{\Delta H^\ddagger}{RT} + \frac{\Delta S^\ddagger}{R}} \tag{18}$$

The Eyring equation of absolute reaction rates may be applied to all types of reactions and permits direct calculation of the reaction velocity constant if the enthalpy and entropy of activation are known or if they can be calculated. It should be noted that the time unit in the reaction velocity constant of Equations (17) and (18) is in reciprocal seconds since it is based upon the frequency expressed in the ratio of **k**/**h**.

Illustration 1. In the dimerization of ethylene at 673°K Glasstone, Laidler, and Eyring[1] report a value of $\Delta H^\ddagger$ equal to 32.73 kcal and $\Delta S^\ddagger$ equal to -35.00 entropy units per mole of butene-1 for standard states of unit fugacity. Assuming ideal behavior:

(*a*) Estimate the value of the reaction velocity constant.

(*b*) Estimate the instantaneous rate of reaction in pound-moles of ethylene converted per cubic foot per hour at 673°K and with ethylene at 2 atm partial pressure.

(*c*) Calculate $\Delta S^\ddagger$ when the standard state is taken as unit mole fraction at 673°K and 2 atm pressure.

When Equation (18) is used, $R' = 0.08206$ (liters) (atm)/(g-mole)(°K). Assume $\nu^\ddagger = 1.0$ and $z_m = 1.0$, then

$$(a)\quad k = \frac{(2.084)10^{10}}{(0.08206)} e^{\frac{-32730}{(1.987)(673)} - \frac{35.00}{1.987}} = 13.35(10^{-8}) \text{ g-mole butene/(liter)(sec)(atm)}^2$$

This constant, expressing the rate of formation of butene, is compared by Glasstone, Laidler, and Eyring with an experimental value of $k'' = 0.0374$ per (atm)(hr) for the rate of conversion of ethylene. The units of this constant result from the expression of reaction rate in terms of the rate of reduction of pressure in atmospheres per hour as the reaction proceeds at constant temperature in a system of constant volume. Thus, if ideal-gas behavior is assumed, $r_u'' = k''p_A^2$ atm per hr. This rate r_u'' is related by the ideal-gas law to r_u the rate in moles/(liter)(hr). Thus, since $n/V = p/R'T$, $r_u = r_u''/R'T$ and $k = k''/R'T$. Since 2 moles of ethylene are converted to 1 mole of butene, the experimental value of k'' is converted to the units of the preceding illustration by the following expression for butene formation:

$$k_{\text{expt}} = \frac{0.0374}{(673)(0.08206)(3600)(2)} = 9.4(10^{-8}) \text{ g-mole/(liter)(sec)(atm)}^2$$

(*b*) $r_u = ka^2 = (13.35)(10^{-8})(2)^2 = 53.4(10^{-8})$ g-mole butene-1/(sec)(liter) or

$$(53.4)(10^{-8})\left(\frac{3600}{454}\right)(28.25)(2) = 2.39(10^{-4}) \text{ lb-mole ethylene/(hr)(cu ft)}$$

(*c*) If the standard state of each component is taken as unit mole fraction then the pressure of each component in its standard state is 2 atm. If ideal behavior is assumed, application of Equation (XI–142) to the reactants and activated complex gives

$$\Delta S_2^\ddagger = \Delta S_1^\ddagger - \Delta n R \ln \frac{p_2}{p_1} = -35.00 - (-1)1.987 \ln 2 = -33.67$$

For ideal-gas behavior the value of $\Delta H^\ddagger$ is not altered with change in standard state.

Ordinarily in the application of Equations (17) and (18) the enthalpy and entropy of activation are assumed to be independent of temperature since the change in heat capacity which accompanies the activation is small. For unimolecular reactions this change is negligible, and $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ may be treated as constants over wide ranges of temperature. This assumption is also satisfactory for other reactions over moderate ranges of temperature. In such cases the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are average values for the temperature range involved.

Where rate data are to be extended over wide temperature ranges the effect of $\Delta C_p^{\ddagger}$, the change in heat capacity accompanying the formation of the activated complex should be considered. Where $\Delta C_p^{\ddagger}$ is constant, Equations (XVI–9 and 10) become

$$\Delta H^{\ddagger} = I_H^{\ddagger} + \Delta C_p^{\ddagger} T \tag{19}$$

$$\Delta S^{\ddagger} = I_S^{\ddagger} + \Delta C_p^{\ddagger} \ln T \tag{20}$$

Equations (19) and (20) are ordinarily used only where rate data are translated to a widely different temperature range, as, for example, if low-temperature rate data in a forward reaction are combined with thermodynamic data in order to estimate rates of the reverse reaction at high temperature. For rate equations in either temperature range $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ may be taken as constant at average values.

If the Eyring equation is used for the interpretation of experimental data it is necessary that rate measurements be available at two temperatures in order to evaluate $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. If $\Delta S^{\ddagger}$ can be approximated by theoretical calculations, rate measurements at one temperature suffice to evaluate reaction rates at other temperatures. By application of the statistical methods developed in Chapter XVI, values of $\Delta S^{\ddagger}$ can be estimated which in many cases are probably as accurate as the average experimental data. Eyring and co-workers[1] have also developed theoretical methods for estimating $\Delta H^{\ddagger}$, but these are uncertain for engineering application at present.

According to the Eyring theory an activated complex must be formed for the reverse reaction which has the same thermodynamic properties as that formed in the forward reaction. Since the forward complex is in equilibrium with reactants and the reverse complex is in equilibrium with the products it follows that the actual over-all rates are determined by the rate of conversion of one complex to the other. Since these two complexes are identical in thermodynamic properties and differ only in the direction in which they are decomposing, it is customary to use but one symbol for both. Thus if Equation (17) is applied to the reverse reaction and the reverse properties are designated with primes, there results,

$$k' = \frac{r'_{*}}{a_R^r a_{\mathbf{S}}^s} = \frac{\mathbf{k}T}{\mathbf{h}\gamma^{\ddagger} v_m} e^{-\frac{\Delta H^{\ddagger\prime}}{RT} + \frac{\Delta S^{\ddagger\prime}}{R}} \tag{21}$$

By combination of (17) and (21) with (4),

$$K = \frac{k}{k'} = e^{-\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}} \tag{22}$$

where

$$\Delta H^\circ = \Delta H^\ddagger - \Delta H^{\ddagger\prime} \tag{23}$$

$$\Delta S^\circ = \Delta S^\ddagger - \Delta S^{\ddagger\prime} \tag{24}$$

ΔH°, ΔS° = standard enthalpy and entropy changes of the over-all reaction

Equation (22) permits evaluation of the velocity constant of the reverse reaction as a function of temperature if that of the forward reaction together with the over-all standard heat and entropy changes of the reaction are known.

The significance of the activated state is clarified by Fig. 167 which indicates the enthalpy changes when reactants at A change to products at B. In order that the reaction may proceed the reactants must be energized to the level corresponding to $H^\ddagger$ by the acquisition of enthalpy of activation $\Delta H^\ddagger$. When the complex decomposes energy $\Delta H^{\ddagger\prime}$ is released to form the products at level B. In order that the reverse reaction may take place an energy of activation $\Delta H^{\ddagger\prime}$ must be acquired so that the molecules may pass over the energy barrier represented by level $H^\ddagger$. The heat of reaction is the difference between the enthalpies of the final and initial states which in Fig. 167 is negative for the forward and positive for the reverse reaction.

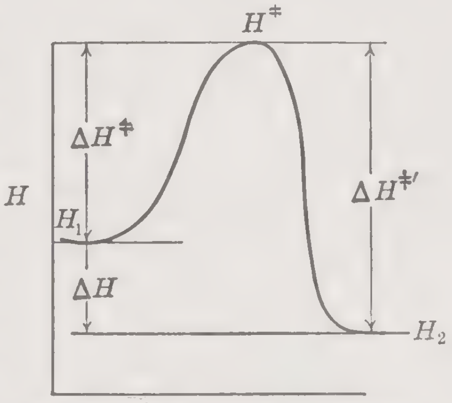

FIG. 167. Enthalpy of Activation.

Illustration 2. Nitric oxide is decomposed according to the following second-order reaction:

$$2NO \rightleftarrows N_2 + O_2$$

The reaction velocity constants as converted from values given in the International Critical Tables are

at $T = 1620°K$, $k = 0.0108$ g-mole/(liter)(sec)(atm)^2
at $T = 1525°K$, $k = 0.0030$

For the reaction $\Delta C_p^\ddagger$ may be taken as -1.0 cal per °K per g-mole of N_2 formed. The fugacity coefficients and compressibility factors may be assumed to be unity.

Calculate:

(a) The values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ at the average experimental temperature of 1572°K.

(*b*) The values of $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, $\Delta H^{\ddagger\prime}$, and $\Delta S^{\ddagger\prime}$ at 2500°K.

(*c*) The values of k and k' at 2500°K.

(*a*) The enthalpy and entropy of activation of the decomposition reactions are evaluated by substitution in Equation (18). Thus, in the specified units,

$$\log \frac{\mathbf{k}}{\mathbf{h}R'} = \log \frac{(1.3805)(10^{-16})}{(6.6240)(10^{-27})(0.08206)} = \log\,(2.540)(10^{11}) = 11.40479$$

Substituting in Equation (18) gives

$$\log 0.0108 = 11.40479 - \frac{\Delta H^{\ddagger}}{(4.576)(1620)} + \frac{\Delta S^{\ddagger}}{4.576} = -1.96658$$

$$\log 0.0030 = 11.40479 - \frac{\Delta H^{\ddagger}}{4.576(1525)} + \frac{\Delta S^{\ddagger}}{4.576} = -2.52288$$

If these are solved simultaneously,

$$\Delta H^{\ddagger} = 66{,}200; \qquad \Delta S^{\ddagger} = -20.323$$

(*b*) From Equation (19) at 1572°K,

$$66{,}200 = I_H^{\ddagger} - 1.0(1572) \quad \text{or} \quad I_H^{\ddagger} = 67{,}772$$

From Equation (20),

$$-20.323 = I_S^{\ddagger} - 1.0 \ln 1572 \quad \text{or} \quad I_S^{\ddagger} = -12.963$$

At 2500°K

$$\Delta H^{\ddagger} = 67{,}772 - 1.0(2500) = 65{,}270$$

$$\Delta S^{\ddagger} = -12.963 - 1.0 \ln 2500 = -20.788$$

From the data of Tables V, XIV and XXXV (pages 214, 253, and 701)

$$\Delta H^{\circ} = -43{,}200 + \int_{291}^{2500} [(0.09 - 0.000391T + (0.169)(10^{-6})T^2]\,dT = -43{,}327$$

$$\Delta S^{\circ} = -5.86 + \int_{298}^{2500} \frac{[(0.09 - 0.000391T + (0.169)(10^{-6})T^2]\,dT}{T} = -6.009$$

$$\Delta G^{\circ}/T = (-43{,}327/2500) + 6.009 = -11.322$$

$$\log K = -\frac{\Delta G^{\circ}}{4.576T} = 2.47421$$

$$K = 298$$

From Equations (23) and (24),

$$\Delta H^{\ddagger\prime} = \Delta H^{\ddagger} - \Delta H^{\circ} = 65{,}270 - (-43{,}327) = 108{,}597$$

$$\Delta S^{\ddagger\prime} = \Delta S^{\ddagger} - \Delta S^{\circ} = -20.788 - (-6.009) = -14.779$$

From Equation (18),

$$k = (2.540)(10^{11})e^{-\frac{65{,}270}{R(2500)} - \frac{20\ 788}{R}} = (2.540)(10^{11})(10^{-10.2481})$$
$$= 14.346$$

$$k' = (2.540)(10^{11})e^{-\frac{108,597}{R(2500)} - \frac{14.779}{R}} = (2.540)(10^{11})(10^{-12.726})$$
$$= 0.0477$$

For verification of agreement with K obtained from $\Delta G°$,

$$K = \frac{k}{k'} = \frac{14.346}{0.0477} = 301$$

In the present state of development of the theory there is room for considerable speculation as to the exact structure of the activated complex in a given reaction. Where the complex is formed from a single molecule it is assumed to be an abnormal structure which has acquired additional bonding energy resulting in deformation and changes of the normal energy levels. The formation of the complex is accompanied by a large absorption of energy and increase in enthalpy, but since the general configuration of the complex is similar to that of the molecule the corresponding change in standard entropy is generally small and may be either positive or negative.

Where the activated complex is formed from two or more molecules new bonds are established with generally a large increase in enthalpy. Since two or more molecules go to form the complex there is a loss in translational entropy, and the over-all standard entropy change accompanying formation of the complex is generally negative. If a single product molecule results, the entropy of the complex is similar to that of the product. Thus, in the dimerization of ethylene discussed in Illustration 1, Glasstone, Laidler, and Eyring[1] assume that the activated complex is a linear molecule having the same entropy as butene-1 but with an enthalpy greater by approximately 57 kcal per g-mole. In the oxidation of nitric oxide by the termolecular reaction $2NO + O_2 = N_2O_4$ the activated complex is assumed to have the structure $O = N—O—O—N = O$ with the bonds of the oxygen atoms at 90° angles and with free rotation about the O—O bond.

Arrhenius Equation. Previous to the development of the Eyring theory of absolute reaction rates the Arrhenius equation was generally used to evaluate the effect of temperature upon the reaction velocity constant. According to Arrhenius a reaction is able to take place when the requisite molecules which collide with each other possess an abnormally high energy content greater than the average content of the corresponding temperature level by an amount termed the *energy of activation, E.* In accordance with the Maxwell–Boltzmann distribution law the fraction of molecules energized to this activated state is equal to $e^{-\frac{E}{RT}}$, and the following expression results

$$k = Ae^{\frac{-E}{RT}} \tag{25}$$

where E = the molal energy of activation
A = proportionality factor characteristic of the system and termed the *frequency factor*

Equation (25) is designated as the Arrhenius equation and has been found to represent the temperature variation of the reaction velocity constants of single reactions with satisfactory accuracy. By comparison of Equations (18) and (25) it may be noted that for gaseous reactions the Arrhenius equation is in agreement with the Eyring equation where $E = \Delta H^{\ddagger}$, and $A = \frac{\mathbf{k}}{\mathbf{h}\nu^{\ddagger} z_m R'} e^{\frac{\Delta S^{\ddagger}}{R}}$. In the general case for nonideal solutions represented by Equation (17) the frequency factor is not temperature independent as assumed in the Arrhenius equation, but there is ordinarily little numerical difference between $\Delta H^{\ddagger}$ and E.

DIFFERENTIAL RATE EQUATIONS

For the *first-order reaction* $A \rightleftarrows R$, Equation (1) for the forward rate may be written as

$$r_u = k a_A \tag{26}$$

Where activities are unity at unit mole fraction $a_A = \gamma_A N_A = \gamma_A (n_A/n_t)$, and Equation (26) becomes

$$r_u = k\gamma_A \frac{n_A}{n_t} = k\gamma_A N_A \tag{27}$$

in which γ_A = activity coefficient of component A
n_A = moles of reactant A present in the system under consideration
n_t = total number of moles in the system under consideration

For gaseous reactions in ideal solutions and where activities are unity at unit fugacity, $a_A = \pi \nu_A N_A = \pi \nu_A (n_A/n_t)$, and $\pi = (z_m n_t R' T)/V$. Substituting in Equation (26) gives

$$r_u = \frac{k\nu_A n_A \pi}{n_t} = \frac{k\nu_A z_m R' T n_A}{V} \tag{28}$$

For ideal gases ν_A and z_m are unity, and Equation (28) becomes

$$r_u^* = \frac{k n_A \pi^*}{n_t} = k p_A^* = \frac{kR' T n_A}{V^*} \tag{29}^*$$

or in a batch system where $r_u = \frac{-dn_A}{Vd\tau}$ and τ = time

$$-\frac{dn_A}{d\tau} = kR'Tn_A \tag{30}^*$$

Integration gives

$$\ln\frac{n_{A0}}{n_A} = kR'T\tau \tag{31}^*$$

where n_{A0} = moles of A initially present when $\tau = 0$. It is evident from Equations (29–31) that for a first-order reaction proceeding in a mixture of ideal gases the extent of conversion of the reactant in a given time interval at constant temperature is independent of pressure or volume while the rate of reaction per unit volume is directly proportional to the first power of the pressure.

For *second-order reactions* of the type $A + B \rightleftarrows R \cdots$ the rate of the forward reaction is expressed by

$$r_u = ka_Aa_B \tag{32}$$

Where activities are unity at unit mole fraction Equation (32) becomes

$$r_u = \frac{k\gamma_An_A\gamma_Bn_B}{n_t^2} \tag{33}$$

For gaseous reactions in ideal solution where activities are equal to fugacities,

$$r_u = \frac{k\nu_A\nu_Bn_An_B\pi^2}{n_t^2} = \frac{k\nu_A\nu_B(z_mR'T)^2n_An_B}{V^2} \tag{34}$$

For ideal gas behavior Equation (34) reduces to

$$r_u^* = \frac{kn_An_B(\pi^*)^2}{n_t^2} = kp_A^*p_B^* = \frac{k(R'T)^2n_An_B}{V^2} \tag{35}^*$$

From Equation (35) it is evident that in mixtures of ideal gases the rate of a second-order reaction is proportional to the square of the pressure or inversely proportional to the square of the volume of the system.

For *third-order reactions* of the type $A + B + C \rightleftarrows R \cdots$ the rate of the forward reaction is expressed by

$$r_u = ka_Aa_Ba_C \tag{36}$$

Where activities are unity at unit mole fraction the rate equation becomes

$$r_u = \frac{k\gamma_An_A\gamma_Bn_B\gamma_Cn_C}{n_t^3} \tag{37}$$

For gaseous reactions which approximate ideal solutions

$$r_u = \frac{k\nu_A\nu_B\nu_C n_A n_B n_C \pi^3}{n_t^3} = \frac{k\nu_A\nu_B\nu_C(z_m R'T)^3 n_A n_B n_C}{V^3} \tag{38}$$

If the gases behave ideally,

$$r_u^* = \frac{k\pi^3 n_A n_B n_C}{n_t^3} = kp_A^* p_B^* p_C^* = \frac{k(R'T)^3 n_A n_B n_C}{V^3} \tag{39}^*$$

From Equation (39) it is evident that in ideal-gaseous systems the rate of a third-order reaction at constant temperature is proportional to the cube of the pressure or is inversely proportional to the cube of the volume of the system.

Homogeneous reactions of higher than the third order are improbable, and it is doubtful that any have been observed; only a few third-order reactions are known.

Simultaneous, Consecutive, and Reverse Reactions. The rate equations thus far discussed are applicable to the effects of single reactions without consideration of other reactions which may be occurring in the system simultaneously. Any one of the typical reactions considered might be accompanied by one or more simultaneous reactions, such as $B + F \rightarrow S$, involving one or more of the same reactants. In such cases the results of the simultaneous reactions are additive, and the rate at which component B is consumed is the sum of the rates of all the reactions in which it is involved. Similarly, if the product of a primary reaction enters into a secondary or consecutive reaction the net rate at which it is formed is the difference between the rates of the primary and secondary reactions. In this manner over-all rate equations may be developed for complex reacting systems. For example, the over-all rate of reaction of reactant A in the consecutive reactions $A + B \rightarrow R$ and $A + R \rightarrow S$ is given by

$$r_u = k_1 a_A a_B + k_2 a_A a_R \tag{40}$$

As developed in Chapter XVI, all reactions are to some degree reversible, and if conditions are such that the rate of the reverse reaction is important its effect must be included in the over-all rate equation. Thus, if we consider a *reversible first-order reaction* of the type $A \rightleftarrows R$, the net rate of reaction of A is expressed by

$$r = ka_A - k'a_R \tag{41}$$

where

k' = reaction velocity constant of the reverse reaction

At equilibrium the net rate of reaction must be zero, and

$$\frac{k}{k'} = \frac{a_R}{a_A} = K \tag{42}$$

where

$$K = \text{equilibrium constant}$$

Combining Equations (41) and (42) gives

$$r = k\left(a_A - \frac{a_R}{K}\right) \tag{43}$$

Similarly, for a reaction of the type $A + B \rightleftarrows R + S$,

$$r = k\left(a_A a_B - \frac{a_R a_S}{K}\right) \tag{44}$$

It should be noted that the *equilibrium constant is equal to the ratio of the reaction velocity constants only where these constants refer to the same chemical steps.* For a complex reaction the over-all equilibrium constant is not related by any simple ratio to the reaction velocity constants of the separate steps.

In Equations (43) and (44) the terms $(a_A - a_B/K)$ and $(a_A a_B - a_R a_S/K)$ express quantitatively the displacement of the reactions from equilibrium and may be looked upon as the driving forces or potentials which cause the reaction to proceed toward equilibrium. These terms are analogous to voltage as the potential causing an electric current to flow while the reaction velocity constant is analogous to the electrical conductance which determines the rate of flow of electricity under a given voltage.

Reactions of Complex Order. By application of Equation (1) to experimentally determined rate data it has been found that many apparently simple reactions do not correspond to a simple order and that exponents other than integers must be employed in the rate equations. Thus, a reaction may have an experimentally determined order of 0, 0.5, or 1.5. Reactions of this type are classified as of *complex order*. It is difficult to assign a definite molecularity to reactions of complex order, and molecularity and order bear no simple relationship to each other. This distinction between order and molecularity must be clearly understood, and it should be recognized that exponents in a rate equation can be determined only from experimental measurements of rates at varying concentrations.

Many theories have been advanced as to the mechanism of reactions of complex order. One of the most useful views is that such a reaction actually consists of a *chain of reactions* involving the formation of intermediate free radicals or atoms which do not appear in the final products in appreciable proportions. For example, the formation of hydrogen iodide from iodine and hydrogen is a simple second-order reaction corresponding to the equation $H_2(g) + I_2(g) \rightleftarrows 2HI$. However, the parallel formation of hydrogen bromide from hydrogen and bromine is of complex order. This may be explained by intermediate dissociations to form atoms resulting in the following six simultaneous and consecutive reactions:

(1) $Br_2 + H_2 \rightleftarrows 2HBr$
(2) $Br_2 \rightleftarrows 2Br$
(3) $H_2 \rightleftarrows 2H$
(4) $H_2 + Br \rightleftarrows HBr + H$
(5) $H + Br \leftrightarrows HBr$
(6) $Br_2 + H \leftrightarrows HBr + Br$

A complete rate equation for the over-all reaction including the effects of all six contributing reaction rates would be so complicated as to be of little value. However, because of the wide variations in magnitude of specific reaction rates, one or two of the reactions in such a sequence may proceed so slowly as to determine the rate of the over-all reaction while others may proceed so rapidly that equilibrium may be assumed to exist at all times. For this reason the over-all rate is generally determined by the rate of one or two of the intermediate reactions and can frequently be expressed by an equation based on these rate-determining steps only. The subject of complex chain reactions is discussed in more detail on page 843.

Rate Equations in Concentration Units. Equation (1) expresses reaction rates in terms of thermodynamically defined activities which are applicable to all types of systems under all conditions. The rate equations developed on this basis have the advantage of a simple relationship to the thermodynamic equilibrium constant which permits the establishment of a single equation which is applicable to the net rate of a reaction when approaching equilibrium from any direction. These equations are recommended for all problems in commercial reactor design where conditions are generally variable and nonideal.

Most of the reaction-rate data which have been gathered in the past have been correlated in terms of the classical law of mass action proposed by Guldberg and Waage in the following form:

$$r = k_c c_A^a c_B^b c_C^c \cdots \tag{45}$$

where

$c_A = n_A/V$ = concentration of A, moles per unit volume
k_c = reaction velocity constant in concentration units

For systems in which activities are taken as unity at unit mole fraction Equation (1) may be written as

$$r = k(\gamma_A c_A)^a(\gamma_B c_B)^b(\gamma_C c_C)^c \cdots (v_m)^{a+b+c \cdots} \tag{46}$$

where v_m = average molal volume of the reacting system

Combining (45) and (46) with this reference state for activities and using consistent units throughout gives

$$k_c = k(\gamma_A^a \gamma_B^b \gamma_C^c) \cdots (v_m)^{a+b+c \cdots} \tag{47}$$

For ideal solutions of gases where activities are taken as unity at unit fugacity, Equation (1) becomes

$$r = k(\nu_A c_A)^a(\nu_B c_B)^b(\nu_C c_C)^c \cdots (z_m R'T)^{a+b+c \cdots} \tag{48}$$

Combining (45) and (48), for gases in ideal solution, and using consistent units throughout yields

$$k_c = k\nu_A^a \nu_B^b \nu_C^c \cdots (z_m R'T)^{a+b+c \cdots} \tag{49}$$

Equations (47) and (49) relate the two reaction velocity constants k and k_c and may be used to calculate one from the other. Equilibrium constants in concentration units corresponding to k_c are also in use to some extent. Thus,

$$K_c = \frac{c_R^r c_S^s \cdots}{c_A^a c_B^b c_C^c \cdots} = \frac{k_c}{k_c'} \tag{50}$$

This equilibrium constant K_c is related to the true thermodynamic equilibrium constant K by the following equation where activities are unity at unit mole fraction:

$$K_c = K \frac{\gamma_A^a \gamma_B^b \gamma_C^c \cdots}{\gamma_R^r \gamma_S^s \cdots} (v_m)^{(a+b+c \cdots)-(r+s \cdots)} \tag{51}$$

Where activities are unity at unit fugacity,

$$K_c = K \frac{\nu_A^a \nu_B^b \nu_C^c \cdots}{\nu_R^r \nu_S^s \cdots} (z_m R'T)^{(a+b+c \cdots)-(r+s \cdots)} \tag{52}$$

In many cases it may be assumed that ideal conditions exist, and the values of γ, ν, and z in Equations (46–52) may be taken as unity.

The widespread use of concentration units in kinetic relationship has resulted from the fact that many laboratory rate measurements have been made at conditions of substantially constant volume. Under these conditions data are determined directly in concentration units, and the resulting rate equations are more simply integrated than if activities are employed. It is convenient to use rate equations in concentration units for the analysis of such laboratory data at constant volume. Thermodynamic reaction velocity constants may then be calculated from Equations (46–52).

In dealing with gaseous-reaction-rate data in concentration units the normal molal volume is frequently used as a unit of volume. Thus, in the metric system concentrations and rates are expressed in terms of gram-moles per 22.41 liters. Concentrations in these units are numerically equal to pound-moles per 359 cu ft. If pressures are expressed in atmospheres, the values of the gas-law constant R' is 1/273 in (atm) (22.41 liters)/(°K)(g-mole) or 1/492 in (atm)(359 cu ft)/(°R)(lb-mole). The normal molal volume may be used exactly like any other unit of volume, but careful designation of units is necessary to avoid confusion. It is a good plan to verify the dimensional consistency of any rate equation by writing it in terms of the units employed and making sure that all cancel.

Illustration 3. A second-order reaction in a system of ideal gases at a temperature of 910°K has a reaction velocity constant $k_c = 70$ liters/(g-mole)(sec). Calculate the reaction velocity constant k in g-moles/(liter)(atm)^2(hr).

Solution: From Equation (49), if k_c is converted to consistent time units,

$$k = \frac{k_c(3600)}{(R'T)^2} = \frac{(70)(3600)}{[(0.08206)(910)]^2} = 45 \frac{\text{g-moles}}{(\text{liter})(\text{atm})^2(\text{hr})}$$

INTEGRAL CONVERSION EQUATIONS

Equations (1) and (45) express the instantaneous rate at which a reaction proceeds as a function of the conditions in the system for a particular infinitesimal interval of time $d\tau$ in a batch process or for an infinitesimal increment of volume dV in a flow process. As the reaction proceeds these conditions change with time in a batch process and with distance traveled in a flow process; as a result the rate of reaction continually changes. In order to evaluate the effects produced during a finite interval of time or in a finite flow reactor it is necessary to integrate the instantaneous rate equations with due consideration of the changes of all variables.

Nonflow Reactions. It is convenient to express the results of a reaction in terms of the extent of conversion of the limiting reactant A. The conversion x_A is defined as the moles of A transformed per unit mass of original reactor charge or feed. Thus,

$$n_A = n_{A0} - x_A \tag{53}$$

$$-dn_A = dx_A \tag{54}$$

where n_{A0}, n_A = the number of moles of A per unit mass of reacting system initially and at any time τ, respectively.

From the definition of reaction rate, in a batch process,

$$r = +\frac{dx_A}{V_c d\tau} \tag{55}$$

where r = moles of A converted per unit time per unit volume of reactor occupied by the reacting system

V_c = volume occupied by the reacting system per unit mass

The integration of Equation (55) requires complete expression of both r and V_c as functions of x_A. The instantaneous rate of reaction r is related to x_A through the differential rate equations of the preceding section.

For a batch or nonflow reaction Equation (55) is integrated directly to obtain the time τ required for a specified extent of conversion x_A. Thus,

$$\tau = \int_0^{x_A} \frac{dx_A}{V_c r} \tag{56}$$

If the reaction is restrained to constant volume and temperature the integration of Equation (56) is readily carried out for reactions of simple order in systems which form ideal solutions. For a first-order reaction in an ideal-liquid system in which the reverse reaction is negligible the rate is expressed by Equation (27) which may be combined with Equations (47) and (56). Thus,

$$\tau = \int_0^{x_A} \frac{n_t dx_A}{V_c k(n_{A0} - x_A)} = \int_0^{x_A} \frac{dx_A}{k_c(n_{A0} - x_A)} \tag{57}$$

where n_t = total number of moles per unit mass of reacting system = V_c/v_m. As previously pointed out, the expression in terms of k_c is more easily integrated. Thus

$$\tau = \frac{1}{k_c} \ln \frac{n_{A0}}{n_{A0} - x_A} \tag{58}$$

By the same procedure integrated equations may be derived from unidirectional second- and third-order reactions and for simple reversible reactions. The results of these integrations, in concentration units, are summarized in Table LII. These equations are directly applicable to either ideal-liquid or gaseous systems under the specified conditions. Integrated equations of this type may also be applied satisfactorily to nonideal systems in which the term involving the activity coefficients does not vary greatly.

TABLE LII

Homogeneous Reaction Rates at Constant Volume for Ideal Solutions at Constant Temperature

r = moles of component A converted per unit time per unit volume
τ = time elapsed
k_c = reaction velocity constant in concentration units
K_c = equilibrium constant in concentration units
n_{A0}, n_{B0} = moles A, B, initially present per unit mass of charge
x_A = moles of A transformed per unit mass of charge
V_c = volume of reacting system in reactor at time τ per unit mass of initial charge
$n_A = n_{A0} - x_A$ = moles of A present at time τ per unit mass of charge

General rate equation: $r = -\dfrac{dn_A}{V_c d\tau}$

Unidirectional Reactions

First Order: $A \rightarrow \nu P$

$$r = \frac{k_c n_A}{V_c}; \qquad \tau = \frac{1}{k_c} \ln \frac{n_{A0}}{n_{A0} - x_A} \tag{a}$$

Second Order: $2A \rightarrow \nu P$

$$r = k_c \left(\frac{n_A}{V_c}\right)^2; \qquad \tau = \frac{V_c}{k_c n_{A0}} \frac{x_A}{(n_{A0} - x_A)} \tag{b}$$

Second Order: $A + B \rightarrow \nu P$

$$r = k_c \frac{n_A n_B}{V_c^2}; \qquad \tau = \frac{V_c}{k_c(n_{A0} - n_{B0})} \ln \left[\frac{n_{B0}(n_{A0} - x_A)}{n_{A0}(n_{B0} - x_A)}\right] \tag{c}$$

Third Order: $3A \rightarrow \nu P$

$$r = k_c \left(\frac{n_A}{V_c}\right)^3; \qquad \tau = \frac{V_c^2 x_A}{2k_c n_{A0}^2} \left[\frac{2n_{A0} - x_A}{(n_{A0} - x_A)^2}\right] \tag{d}$$

Third Order: $2A + B \rightarrow \nu P$

$$r = k_c \frac{n_A^2 n_B}{V_c^3}; \qquad \tau = \frac{V_c^2}{k_c(n_{B0} - \frac{1}{2}n_{A0})} \left[\frac{x_A}{n_{A0}(n_{A0} - x_A)} + \frac{1}{n_{A0} - 2n_{B0}} \ln \left[\frac{n_{A0}(n_{B0} - \frac{1}{2}x_A)}{n_{B0}(n_{A0} - x_A)}\right]\right. \tag{e}$$

Third Order: $A + B + C \rightarrow \nu P$

$$r = k_c \frac{n_A n_B n_C}{V_c^3};$$

$$\tau = \frac{V_c^2}{k_c} \left[\frac{1}{AC} \ln \frac{n_{A0}}{n_{A0} - x_A} + \frac{1}{AB} \ln \frac{n_{B0}}{n_{B0} - x_A} + \frac{1}{BC} \ln \frac{n_{c0}}{n_{c0} - x_A}\right] \tag{f}$$

where $A = n_{B0} - n_{A0}$; $B = n_{B0} - n_{C0}$; $C = n_{C0} - n_{A0}$

Reversible Reactions

First Order: $A \rightleftarrows R$

$$r = \frac{k_c}{V_c}\left(n_A - \frac{n_B}{K_c}\right); \qquad \tau = \frac{K_c}{k_c(K_c + 1)} \ln \left[\frac{K_c n_{A0} - n_{R0}}{K_c n_{A0} - n_{R0} - (K_c + 1)x_A}\right] \tag{g}$$

For various types of second-order and mixed second-first order reversible reactions τ may be expressed by Equation (h). The constants a, b, c, and q are defined in each case.

$$q = 4ac - b^2$$

where

$$q < 0; \qquad \tau = \frac{V_cK_c}{k_c}\left[\frac{1}{\sqrt{-q}} \ln\left[\frac{(2cx_A + b - \sqrt{-q})(b + \sqrt{-q})}{(2cx_A + b + \sqrt{-q})(b - \sqrt{-q})}\right]\right] \tag{h}$$

First and Second Order:

$A \rightleftarrows 2R$

$$\left.\begin{aligned} a &= V_cK_cn_{A0} - n_{R0}^2 \\ b &= -K_cV_c - 4n_{R0} \\ c &= -4 \end{aligned}\right\} \qquad \text{(i)}$$

$A + B \rightleftarrows R$

$$\left.\begin{aligned} a &= K_cn_{A0}n_{B0} - V_cn_{R0} \\ b &= -K_cn_{B0} - K_cn_{A0} - V_c \\ c &= K_c \end{aligned}\right\} \qquad \text{(j)}$$

$A \rightleftarrows R + S$

$$\left.\begin{aligned} a &= V_cK_cn_{A0} - n_{R0}n_{S0} \\ b &= -V_cK_c - n_{S0} - n_{R0} \\ c &= -1 \end{aligned}\right\} \qquad \text{(k)}$$

$2A \rightleftarrows R$

$$\left.\begin{aligned} a &= K_cn_{A0}^2 - V_cn_{R0} \\ b &= -2K_cn_{A0} - \frac{V_c}{2} \\ c &= K_c \end{aligned}\right\} \qquad \text{(l)}$$

Second Order:

$A + B \rightleftarrows R + S$

$$\left.\begin{aligned} a &= K_cn_{A0}n_{B0} - n_{R0}n_{S0} \\ b &= -K_cn_{B0} - K_cn_{A0} - n_{R0} \\ &\quad - n_{S0} \\ c &= K_c - 1 \end{aligned}\right\} \qquad \text{(m)}$$

$A + B \rightleftarrows 2R$

$$\left.\begin{aligned} a &= K_cn_{A0}n_{B0} - n_{R0}^2 \\ b &= -K_cn_{A0} - K_cn_{B0} - 4n_{R0} \\ c &= K_c - 4 \end{aligned}\right\} \qquad \text{(n)}$$

$2A \rightleftarrows R + S$

$$\left.\begin{aligned} a &= K_cn_{A0}^2 - n_{R0}n_{S0} \\ b &= -2K_cn_{A0} - \frac{n_{R0}}{2} - \frac{n_{S0}}{2} \\ c &= K_c - \tfrac{1}{4} \end{aligned}\right\} \qquad \text{(o)}$$

$2A \rightleftarrows 2R$

$$\left.\begin{aligned} a &= K_cn_{A0}^2 - n_{R0}^2 \\ b &= -2K_cn_{A0} - 2n_{R0} \\ c &= K_c - 1 \end{aligned}\right\} \qquad \text{(p)}$$

In using rate equations care must be exercised to use consistent units throughout. Thus, in the equations of Table LII it is important that the unit of volume on which the reaction rate is based is the same unit of volume on which concentrations are based and that the value of k_c is consistent with this volume.

Illustration 4. Sulfuryl chloride vapors are heated in a closed vessel for 30 min at 610°F and 1 atm initial pressure. The dissociation of SO_2Cl_2 to SO_2 and Cl_2 is a reaction of the first order and not influenced by the walls of the vessel. The reverse reaction is negligible. The reaction velocity constant k_c is 0.00132 per min.

Calculate:

(*a*) The percentage decomposition of SO_2Cl_2.

(*b*) The weight of SO_2 formed from 1 cu meter of SO_2Cl_2 at the initial conditions in 30 min.

(*c*) The time required to decompose 90 per cent of the SO_2Cl_2.

(*a*) Let n_{A0} = kg-moles of SO_2Cl_2 initially present in the constant volume of reacting system

x_A = kg-moles of SO_2Cl_2 transformed in time τ

From Equation (a), Table LII,

$$\tau = \frac{1}{k_c} \ln \frac{n_{A0}}{n_{A0} - x_A}$$

$$30 = \frac{1}{0.00132} \ln \frac{n_{A0}}{n_{A0} - x_A}$$

$$1 - \frac{x_A}{n_{A0}} = 0.9612$$

Hence the percentage decomposition of SO_2Cl_2 = (1 − 0.9612)100 = 3.88 per cent

(*b*) SO_2Cl_2 initially present per cubic meter $= \dfrac{1}{22.41} \dfrac{(273)}{(1070)} = 0.0205$ kg-mole

Weight of SO_2 formed = (0.0388)(0.0205)(64) = 0.0512 kg

(*c*) For 90 per cent decomposition, $x_A = 0.9n_{A0}$

$$\ln \frac{n_{A0}}{0.1n_{A0}} = 0.00132\tau$$

Hence, τ = 1740 min.

Illustration 5. The decomposition of nitrous oxide proceeds as a second-order reaction, $2N_2O \rightarrow 2N_2 + O_2$. The reverse reaction is negligible. At 895°C the value of k_c is given by the International Critical Tables as 977 where concentrations are expressed in gram-moles per cubic centimeter and time in seconds. If pure N_2O at an initial pressure of 1 atm is heated at 895°C in an autoclave of constant volume, calculate the time required for 90 per cent decomposition.

In Equation (b), Table LII, V_c = 22,410 (1168/273) = 96,000 cc

$$n_{A0} = 1.0; \qquad x_A = 0.9$$

$$\tau = \left(\frac{96{,}000}{977}\right)\left(\frac{0.9}{0.1}\right) = 884 \text{ sec}$$

In Illustrations 4 and 5 it was assumed that the rate of the reverse reaction was in all cases negligible. Where this is not the case the net rate of reaction is obtained as the difference between the rates of the forward and reverse reactions. In Table LII are classified the differential and integrated rate equations for several types of simple reversible reaction at constant temperature and volume. For a reversible reaction which is first order in both directions volume terms do not enter indicating that the extent of conversion in a given time is independent of pressure and volume. The integrated equations for reversible reactions which proceed with no change in number of moles apply to all isothermal conditions whether at constant volume or constant pressure, whether batch or flow types.

Illustration 6. The hydrolysis of methyl acetate is a reaction of the second order, proceeding according to the equation:

$$CH_3COOCH_3 + H_2O \leftrightarrows CH_3COOH + CH_3OH$$

This reaction is catalyzed by the presence of hydrogen ions. In a normal solution of HCl at 25°C the velocity coefficient of the forward reaction is $k_c = 0.0001482$, and that of the reverse reaction is $k_c' = 0.000677$ liter/(g-mole)(min). The initial concentration of such a solution is $n_{A0} = 1.151$ g-moles of methyl acetate per liter and $n_{B0} = 48.76$ g-moles of water per liter. No alcohol nor acetic acid is initially present. On the basis of 1.0 liter of solution, calculate:

(*a*) The moles and percentage of ester transformed in 60 min.

(*b*) The moles and percentage of ester transformed at equilibrium.

(*c*) The moles and percentage of ester transformed in 60 min if the reverse reaction and the change in concentration of water are neglected. This in effect is treating the hydrolysis as though it were a unidirectional first-order reaction.

(*a*) In Equations (h) and (m) of Table LII:

$$K_c = \frac{k_c}{k_c'} = \frac{0.0001482}{0.000677} = 0.219$$

$k_c = 0.0001482$ liter/(g-mole)(min)

$n_{A0} = 1.151$ g-mole per liter

$n_{B0} = 48.76$ g-mole per liter

$n_{R0} = 0$

$n_{S0} = 0$

$x_A =$ g-moles ester converted

$V_c = 1.0$ liter

$a = K_c n_{A0} n_{B0} - n_{R0} n_{S0} = (0.219)(1.151)(48.76) = 12.29$ (g-moles)^2/(liter)^2

$b = -K_c n_{A0} - K_c n_{B0} - n_{R0} - n_{S0}) = (0.219)(-1.151 - 48.76) = -10.93$ g-moles per liter

$c = K_c - 1 = -0.7811$

$q = 4ac - b^2 = (4)(12.29)(-0.7811) - (10.93)^2 = -157.9$ (g-moles)^2/(liter)^2

$\sqrt{-q} = 12.57$ g-moles per liter

Substituting in Equation (h) gives

$$60 = \frac{(0.2189)}{0.0001482}\left\{\frac{2.303}{12.57}\left[\log\left(\frac{2(-0.7811x_A) - 10.93 - 12.57}{2(-0.7811x_A) - 10.93 + 12.57}\right)\left(\frac{(-10.93 + 12.57)}{(-10.93 - 12.57)}\right)\right]\right\}$$

$$\log\frac{(0.110x_A + 1.65)}{(-1.562x_A + 1.65)} = 0.2217$$

or

$$2.712x_A = 1.099$$
$$x_A = 0.405$$

Percentage conversion of ester $= (0.405/1.151)(100) = 35.2$ per cent

(*b*) At equilibrium:

$$\frac{x_A^2}{(1.151 - x_A)(48.76 - x_A)} = 0.219$$
$$x_A = 1.04$$

Percentage conversion $= (1.04/1.151)(100) = 90.5$ per cent (*c*) If the reverse reaction and removal of water are neglected, the differential rate equation may be written as $-(dn_A)/(n_A) = (k_c n_B d\tau)/(V_c)$ or

$$\frac{dx_A}{n_{A0} - x_A} = \frac{k_c n_{B0} d\tau}{V_c}$$

Integration yields

$$\ln \frac{n_{A0}}{n_{A0} - x_A} = \frac{k_c n_{B0} \tau}{V_c}$$

$$\ln \frac{1.151}{(1.151 - x_A)} = (48.76)(0.0001482)(60)$$

$$x_A = 0.405 \text{ g-moles}$$

$$\text{Percentage conversion} = \left(\frac{0.405}{1.151}\right)(100) = 35.2 \text{ per cent}$$

From the results of parts (*a*) and (*c*) of Illustration 6 it may be noted that little error is involved in assuming that the reaction follows a first-order mechanism. This results from the fact that the water is present in such great excess that changes in its activity or concentration are negligible. Reactions of higher order under conditions which permit their treatment as first order are termed *pseudo-first-order* reactions. Many systems of industrial importance are of this type and may be handled with satisfactory accuracy on the basis of assumed pseudo mechanism. This procedure frequently results in considerable simplification of calculations but must be used with great care and recognition of the possible errors involved.

Simultaneous Reactions. The simplest case of simultaneous reactions is that of an irreversible first-order reaction in which the reactant A simultaneously reacts in two ways. Thus,

(1) $A \rightarrow R$
(2) $A \rightarrow S$

The over-all rate of decomposition of A is the sum of the rates of the two reactions which may be considered separately. If y_A and z_A represent the moles of A decomposed per unit mass of feed by reactions 1 and 2, respectively, and $x_A = y_A + z_A$, from Equation (45),

$$dy_A = k_{c1}(n_{A0} - y_A - z_A)\, d\tau \tag{59}$$

$$dz_A = k_{c2}(n_{A0} - y_A - z_A)\, d\tau \tag{60}$$

$$dx_A = dy_A + dz_A = (k_{c1} + k_{c2})(n_{A0} - x_A)\, d\tau \tag{61}$$

Combining (59) and (60), where y_A and z_A are 0 at $\tau = 0$ gives

$$\frac{y_A}{z_A} = \frac{k_{c1}}{k_{c2}} \quad \text{or} \quad y_A = \frac{x_A}{\dfrac{k_{c2}}{k_{c1}} + 1} \tag{62}$$

By integrating (61) an expression is obtained for the time τ corresponding to a total conversion x_A in a reaction at constant temperature and volume.

$$\tau = \left(\frac{1}{k_{c1} + k_{c2}}\right) \ln \frac{n_{A0}}{n_{A0} - x_A} \tag{63}$$

Equations (62) and (63) permit complete calculation of the decomposition products formed at any time.

Similar simple integrated equations can be developed for simultaneous second- or third-order irreversible reactions in which the reactants for both reactions are the same and they combine in the same proportions. However, in the general case where the simultaneous reactions involve different reactants, complex simultaneous equations are obtained which are generally best integrated graphically.

Consecutive Reactions. The simplest example of consecutive reactions is the successive unimolecular conversion of reactant A, first to product R and then to S.

$$A \underset{k_{c_1}}{\longrightarrow} R \underset{k_{c_2}}{\longrightarrow} S \tag{64}$$

Where a group of simultaneous or consecutive reactions involves no reactant which is common to all reactions, it is not possible to set up rate equations in terms of the extent of conversion of a limiting reactant, as was done in the development of the preceding rate equations. Instead the equations must be expressed in terms of the concentrations of the individual reactants present at any time. Thus, for the reaction of Equation (64),

$$-\frac{dn_A}{d\tau} = k_{c1}n_A \tag{65}$$

$$-\frac{dn_R}{d\tau} = k_{c2}n_R - k_{c1}n_A \tag{66}$$

$$\frac{dn_S}{d\tau} = k_{c2}n_R \tag{67}$$

where n_A, n_R, n_S = moles of A, R, and S present per unit mass of original charge

An expression for n_A in terms of τ and n_{A0}, is obtained by rearranging Equation (a) of Table LII. Thus:

$$n_A = n_{A0}e^{-k_{c1}\tau} \tag{68}$$

Substituting (68) in (66) gives

$$-\frac{dn_R}{d\tau} = k_{c2}n_R - k_{c1}n_{A0}e^{-k_{c1}\tau} \tag{69}$$

Solution of this linear differential equation gives[2,3]

$$n_R = \frac{n_{A0}k_{c1}}{k_{c2} - k_{c1}} \left(e^{-k_{c1}\tau} - e^{-k_{c2}\tau}\right) \tag{70}$$

Equations (68) and (70) permit evaluation of the quantities of A and R present at any time τ. The corresponding quantity of S is obtained from the material balance.

$$n_S = n_{A0} - n_A - n_R \tag{71}$$

If the reactions considered are reversible to a significant extent, Equation (64) is written

$$A \overset{k_{c1}}{\rightleftarrows} R \overset{k_{c2}}{\rightleftarrows} S \tag{72}$$

Then, from Equation (43),

$$r_A V = \frac{-dn_A}{d\tau} = k_{c1}\left(n_A - \frac{n_R}{K_{c1}}\right) \tag{73}$$

$$-\frac{dn_R}{d\tau} = k_{c2}\left(n_R - \frac{n_S}{K_{c2}}\right) - k_{c1}\left(n_A - \frac{n_R}{K_{c1}}\right)$$

$$= n_R\left(k_{c2} + \frac{k_{c1}}{K_{c1}}\right) - \frac{n_S k_{c2}}{K_{c2}} - n_A k_{c1} \tag{74}$$

Differentiating (73) with respect to time gives

$$\frac{d^2 n_A}{d\tau^2} = -k_{c1}\frac{dn_A}{d\tau} + \frac{k_{c1}}{K_{c1}}\frac{dn_R}{d\tau} \tag{75}$$

substituting Equation (74) in (75) yields

$$\frac{d^2 n_A}{d\tau^2} = -k_{c1}\frac{dn_A}{d\tau} - \frac{k_{c1}}{K_{c1}}\left(k_{c2} + \frac{k_{c1}}{K_{c1}}\right) n_R + \frac{k_{c1}k_{c2}}{K_{c1}K_{c2}}\, n_S$$

$$+ \frac{k_{c1}^2}{K_{c1}}\, n_A \tag{76}$$

From Equation (73), n_R may be expressed in terms of n_A, and, from a material balance,

$$n_S = n_{A0} - n_R - n_A \tag{77}$$

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[2] I. S. and E. S. Sokolnikoff, "Higher Mathematics for Engineers and Physicists," McGraw-Hill Book Company (1934).

[3] T. K. Sherwood and C. E. Reed, "Applied Mathematics in Chemical Engineering," McGraw-Hill Book Company (1939).

If values of n_S from (77) and n_R from Equation (73) are substituted in (74),

$$\frac{d^2n_A}{d\tau^2} + \left(k_{c1} + \frac{k_{c1}}{K_{c1}} + k_{c2} + \frac{k_{c2}}{K_{c2}}\right)\frac{dn_A}{d\tau} + \left(k_{c1}k_{c2} + \frac{k_{c1}k_{c2}}{K_{c1}K_{c2}} + \frac{k_{c1}k_{c2}}{K_{c2}}\right)n_A - \left(\frac{k_{c1}k_{c2}}{K_{c1}K_{c2}}\right)n_{A0} = 0 \qquad (78)$$

This second-order differential equation may be solved[2,3] to give

$$n_A = C_1e^{-D_1\tau} + C_2e^{-D_2\tau} + \frac{k_{c1}k_{c2}}{K_{c1}K_{c2}\,E_2} \qquad (79)$$

for the boundary conditions that $\tau = 0$, $n_A = 1$, $n_R = 0$, $n_S = 0$, $\frac{dn_S}{d\tau} = 0$ where,

$$C_1 = \frac{k_{c1} - D_2C_2}{D_1}$$

$$C_2 = \frac{1 - \dfrac{k_{c1}}{D_1} - \dfrac{k_{c1}k_{c2}}{K_{c1}K_{c2}E_2}}{1 - \dfrac{D_2}{D_1}}$$

$$D_1 = \frac{-E_1 + \sqrt{E_1^2 - 4E_2}}{2}$$

$$D_2 = \frac{-E_1 - \sqrt{E_1^2 - 4E_2}}{2}$$

$$E_1 = k_{c1}\left(1 + \frac{1}{K_{c1}}\right) + k_{c2}\left(1 + \frac{1}{K_{c2}}\right)$$

$$E_2 = k_{c1}k_{c2}\left(1 + \frac{1}{K_{c1}K_{c2}}\right) + \frac{k_{c1}k_{c2}}{K_{c2}}$$

Although the reaction under consideration is of a simple type, Equation (79) is complex and difficult to apply. For the more complicated combinations of higher-order consecutive and simultaneous reactions which are commonly encountered in industrial operations analytical integration may not be possible or practicable. For these problems, which are generally complicated by varying reaction conditions, graphical or trial integration procedures are preferable, as discussed in following sections.

Flow Reactions. The time of reaction in a flow system may be visualized as the time required for an infinitesimal mass of charge to pass through the reactor in an imaginary compartment which moves with the stream and adjusts itself to the temperature, pressure, and composition of the stream. Although in a nonflow process time of reaction is a significant and convenient variable which can be directly measured by a chronometer, it is evident that a flow reaction presents an entirely different problem in which time of reaction cannot be directly measured and is not a convenient variable for correlation of rate data. Much confusion has resulted from improper attempts to interpret data from flow systems on the basis of reaction times which are frequently calculated on the basis of unsound approximations. A rigorous treatment, with all reference to time of reaction omitted, is both more simple and more accurate whenever only a single fluid phase is present. This treatment assumes that diffusion in the direction of flow is negligible and that the stream of reactants moves progressively through the reactor without longitudinal mixing. This condition is closely approached in all commercial and properly designed laboratory reactors except in relatively large-diameter adiabatic reactors, such as are discussed on page 864.

The pertinent problem in the design or analysis of a flow process is the relationship between the reactor volume and the feed rate. This may be arrived at by consideration of an elementary reactor volume dV_r having the cross-sectional area of the reactor and a length dZ in the direction of flow.

Under steady-state conditions the number of moles of A converted in this elementary section per unit time is constant and equal to $r dV_r$. The material balance of the section requires that this conversion equals the reduction in the number of moles of A in the stream passing through the section. Thus,

$$r dV_r = F\,dx_A \tag{80}$$

where

r = rate of reaction, moles of A converted per unit volume of reacting system per unit time
V_r = reactor volume occupied by reacting fluid system
F = reactor feed rate, mass per unit time
x_A = moles of A converted per unit mass of reactor feed

The reactor volume required for a specified conversion x_A is obtained by integration of (80) for a constant feed rate F.

$$\frac{V_r}{F} = \int_0^{x_A} \frac{dx_A}{r} \tag{81}$$

The reaction rate r for a feed of fixed composition processed at constant conditions of temperature and pressure is a function only of conversion x. Thus, under these conditions Equation (81) expresses a relationship between V_r/F and x which is independent of reactor size, shape, or feed rate as long as longitudinal diffusion is negligible. For this reason it is applicable either to following the progressive changes in composition through a reactor operating at steady-state conditions or to correlating data from a series of runs in which V_r/F is varied by varying the feed rate to a reactor of fixed volume operating at constant temperature and pressure.

The integral of Equation (81) may be evaluated analytically for simple reactions under constant pressure and temperature. For example, the rate of a unidirectional first-order reaction in an ideal solution of gases is given by Equation (28). Combining this with (81) gives

$$\frac{V_r}{F} = \frac{1}{\pi k} \int_0^{x_A} \frac{n_t \, dx_A}{\nu_A n_A} \tag{82}$$

where,

n_t = total moles of reacting system per unit mass in the section dV_r

n_A = moles of reactant A per unit mass of reacting system in the section dV_r

Before the integration can be completed n_t and n_A must be expressed as functions of x_A. If δ is the increase in the number of moles in the reacting system per mole of reactant A converted,

$$n_t = n_0 \left(1 + \frac{\delta x_A}{n_0}\right) = n_0(1 + \omega x_A) \tag{83}$$

where

n_0 = total moles of initial feed per unit mass, or the reciprocal of the average molecular weight of the feed

δ = increase in the number of moles of the system per mole of A converted = $[(r + s \cdots) - (a + b \cdots)]/a$ for the general reaction of Equation (5)

ω = δ/n_0, a constant for a particular system

Combining (53), (82), and (83), gives

$$\frac{V_r}{F} = \frac{n_0}{\pi k \nu_A} \int_0^{x_A} \frac{(1 + \omega x_A)}{(n_{A0} - x_A)} \, dx_A \tag{84}$$

Integrating where ν_A is constant yields

$$\frac{V_r}{F} = \frac{n_0}{\pi k \nu_A} \left[-\omega x_A + (1 + \omega n_{A0}) \ln \frac{n_{A0}}{n_{A0} - x_A} \right] \tag{85}$$

By this procedure the integrated equations summarized in Table LIII were developed. As written, the equations are directly applicable to systems of ideal gases. If the term π is omitted they are applicable

TABLE LIII

HOMOGENEOUS REACTION RATES AT CONSTANT PRESSURE AND TEMPERATURE

Flow Reactions

$$aA + bB = rR + sS$$

r = moles of component A converted per unit time per unit volume
n_A = moles of A unconverted per unit mass of feed
n_0 = moles of feed per unit mass of feed
n_t = moles of reacting system per unit mass of feed $= n_0(1 + \omega x_A)$
V_r = volume of reactor occupied by reacting system
F = feed rate, mass per unit time
$n_{A0}, n_{B0}, n_{R0}, n_{S0}$ = moles of components A, B, R, S, respectively, per unit mass of entering feed
x_A = moles of A converted per unit mass of feed
$n_A = n_{A0} - x_A$
σ = ratio of moles of B to moles of A in stoichiometric equation
ν = moles of product in stoichiometric equation

$$\delta = \frac{r + s - a - b}{a}$$

$$\omega = \frac{\delta}{n_0}$$

k = reaction velocity constant
K = equilibrium constant
π = total pressure

General rate equation:

$$r = -F\frac{dn_A}{dV_r}$$

Irreversible Reactions

First Order: $A \rightarrow \nu R$; $\delta = \nu - 1$

$$r = k\frac{n_A\pi}{n_t}; \qquad \frac{V_r}{F} = \frac{n_0}{k\pi}\left[-\omega x_A + (1 + \omega n_{A0}) \ln \frac{n_{A0}}{n_{A0} - x_A}\right] \tag{a}$$

Second Order: General Solution:

$$\frac{V_r}{F} = \frac{n_0^2}{k\pi^2}\left[Hx_A + J\frac{x_A}{n_{A0}(n_{A0} - x_A)} + M \ln\left(\frac{n_{A0}}{n_{A0} - x_A}\right) + N \ln\left(\frac{n_{B0}}{n_{B0} - x_A}\right)\right] \tag{b}$$

Case 1. $2A \rightarrow \nu R; \qquad \delta = \dfrac{\nu - 2}{2}$

$$r = k\left(\frac{n_A \pi}{n_t}\right)^2 \qquad \begin{aligned} H &= \omega^2 \\ J &= (1 + \omega n_{A0})^2 \\ M &= -2\omega(1 + \omega n_{A0}) \\ N &= 0 \end{aligned} \tag{c}$$

Case 2. $A + B \rightarrow \nu R \qquad \delta = \nu - 2$

$$r = k\left(\frac{n_A n_B \pi^2}{n_t^2}\right) \qquad \left.\begin{aligned} H &= \omega^2 \\ J &= 0 \\ M &= -\frac{(1 + \omega n_{A0})^2}{n_{A0} - n_{B0}} \\ N &= \frac{(1 + \omega n_{B0})^2}{n_{A0} - n_{B0}} \end{aligned}\right\} \tag{d}$$

Third Order: General Solution:

$$\frac{V_r}{F} = \frac{n_0^3}{k\pi^3}\left[H x_A + J \frac{x_A}{n_{A0}(n_{A0} - x_A)} + M \ln \frac{n_{A0}}{n_{A0} - x_A} + N \ln \frac{n_{B0}}{n_{B0} - \sigma x_A} \right.$$
$$\left. + Q \ln \frac{n_{c0}}{n_{c0} - x_A} + P \frac{x_A(2n_{A0} - x_A)}{n_{A0}^2(n_{A0} - x_A)^2}\right] \tag{e}$$

Case 1. $3A \rightarrow \nu R \quad \delta = \dfrac{\nu - 3}{3}$

$$r = k\left(\frac{\pi n_A}{n_t}\right)^3 \quad \left\{\begin{array}{ll} \sigma = 1 & \\ H = -\omega^3 & N = 0 \\ J = -3\omega(1 + \omega n_{A0})^2 & Q = 0 \\ M = 3\omega^2(1 + \omega n_{A0}) & P = \frac{1}{2}(1 + \omega n_{A0})^3 \end{array}\right\} \tag{f}$$

Case 2. $2A + B \rightarrow \nu R; \qquad \delta = \dfrac{\nu - 3}{2}$

$$r = k\left(\frac{\pi^3 n_A^2 n_B}{n_t^3}\right)\left\{\begin{array}{ll} \sigma = \frac{1}{2} & \\ H = -2\omega^3 & N = -\dfrac{2(1 + 2\omega n_{B0})^3}{(2n_{B0} - n_{A0})^2} \\ J = \dfrac{2(1 + \omega n_{A0})^3}{2n_{B0} - n_{A0}} & Q = 0 \\ M = \dfrac{2(1 + \omega n_{A0})^2(2\omega n_{A0} - 6\omega n_{B0} - 1)}{(2n_{B0} - n_{A0})^2} & P = 0 \end{array}\right\} \tag{g}$$

Case 3. $A + B + C \rightarrow \nu R; \qquad \delta = \nu - 3$

$$r = k\left(\frac{\pi^3 n_A n_B n_C}{n_t^3}\right)$$

When $n_{A0} = n_{B0}$, use Equation (g).

When $n_{A0} = n_{B0} = n_{C0}$, use Equation (f).

$$\left.\begin{cases} \sigma = 1 & N = -\dfrac{(1 + \omega n_{B0})^3}{(n_{A0} - n_{B0})(n_{B0} - n_{C0})} \\ H = -\omega^3 & \\ J = 0 & Q = \dfrac{(1 + \omega n_{C0})^3}{(n_{A0} - n_{C0})(n_{B0} - n_{C0})} \\ M = \dfrac{(1 + \omega n_{A0})^3}{(n_{A0} - n_{B0})(n_{A0} - n_{C0})} & P = 0 \end{cases}\right\} \quad \text{(h)}$$

Reversible Reactions

First Order: $A \rightleftarrows R \quad (\omega = 0)$

$$r = \frac{k\pi}{n_t}\left(n_A - \frac{n_R}{K}\right); \quad \frac{Vr}{F} = \frac{Kn_0}{(1 + K)k\pi} \ln \frac{P}{P - x_A} \qquad \text{(i)}$$

where
$$P = \frac{Kn_{A0} - n_{R0}}{1 + K}$$

Mixed First and Second Orders: The constants a, b, c, and q are defined in each case.

$$q = b^2 - 4ac, \quad \text{and} \quad q < 0$$

General Case.

$$\frac{V_r}{F} = \frac{Kn_0^2}{k\pi}\left[-\frac{\omega^2}{c}x_A + U \ln\left(\frac{a + bx_A + cx_A^2}{a}\right)\right.$$
$$\left. + \frac{V}{\sqrt{-q}} \ln\left[\frac{(2cx_A + b - \sqrt{-q})}{(2cx_A + b + \sqrt{-q})}\,\frac{(b + \sqrt{-q})}{(b - \sqrt{-q})}\right]\right] \qquad \text{(j)}$$

For $q < 0$

$$U = \frac{\omega(b\omega - 2c)}{2c^2}; \qquad V = \frac{\omega^2 a}{c} - (1 + bU) \qquad \text{(k)}$$

Case 1. $A \rightleftarrows R + S$

$$r = k\left(\frac{\pi n_A}{n_t} - \frac{\pi^2 n_R n_S}{Kn_t^2}\right) \qquad \left.\begin{aligned} a &= \pi n_{R0} n_{S0} - Kn_0 n_{A0} \\ b &= Kn_0(1 - \omega n_{A0}) + \pi(n_{R0} + n_{S0}) \\ c &= K\omega n_0 + \pi \end{aligned}\right\} \qquad \text{(l)}$$

Case 2. $A + B \rightleftarrows R$

$$r = k\left(\frac{\pi^2 n_A n_B}{n_t^2} - \frac{\pi n_R}{Kn_t}\right) \qquad \left.\begin{aligned} a &= n_0 n_{R0} - K\pi n_{A0} n_{B0} \\ b &= K\pi(n_{A0} + n_{B0}) + n_0(1 + \omega n_{R0}) \\ c &= \omega n_0 - K\pi \end{aligned}\right\} \qquad \text{(m)}$$

Case 3. $A \rightleftarrows 2R$

$$r = k\left(\frac{\pi n_A}{n_t} - \frac{\pi^2 n_R^2}{Kn_t^2}\right) \qquad \left.\begin{aligned} a &= \pi n_{R0}^2 - Kn_0 n_{A0} \\ b &= Kn_0(1 - \omega n_{A0}) + 4\pi n_{R0} \\ c &= K\omega n_0 + 4\pi \end{aligned}\right\} \qquad \text{(n)}$$

Case 4. $2A \rightleftarrows R$

$$r = k\left(\frac{\pi^2 n_A^2}{n_t^2} - \frac{\pi n_R}{Kn_t}\right) \qquad \left.\begin{aligned} a &= n_0 n_{R0} - K\pi n_{A0}^2 \\ b &= 2K\pi n_{A0} + n_0(\tfrac{1}{2} + \omega n_{R0}) \\ c &= \tfrac{1}{2}\omega n_0 - K\pi \end{aligned}\right\} \qquad \text{(o)}$$

Second Order: $(\omega = 0)$. The solution is given by equations (j) and (k). To determine the constants a, b, c, use the negatives of the values of a, b, c given in Table LII for the similar cases as follows:

$A + B \rightleftarrows R + S$	Equations (m) of LII
$A + B \rightleftarrows 2R$	Equations (n) of LII
$2A \rightleftarrows R + S$	Equations (o) of LII
$2A \rightleftarrows 2R$	Equations (p) of LII

or use the solution (h) of LII directly, with the values of a, b, c given by equations (m), (n), (o), or (p), Table LII, and with τ in (h) replaced by $\dfrac{V_r}{FV_c}$ and $k_c = k(R'T)^2$.

to liquid systems forming ideal solutions. For nonideal solutions the products of the fugacity or activity coefficients must be included as in Equation (84).

The equations of Table LIII may be used for the evaluation of reaction velocity constants from experimental data or for the design of reactor systems, at constant temperature and pressure, without the consideration of reaction time. Velocity constants evaluated in this manner from flow data may be used for the design of batch processes, or, conversely, velocity constants derived from laboratory batch experiments may be used for the design of flow processes. If for any reason it is desired to calculate the time of reaction in a flow process a separate integration of Equation (56) under suitable conditions of restraint is required. In the special case of a reaction at constant temperature and pressure which produces no change in the number of moles of the system, $\tau = V_r\rho_f/F$, and the equations of both Tables LII and LIII are applicable.

It should be noted that V_r is the volume of the reactor actually occupied by the reacting fluid. Where the inside of a reactor is partly occupied by inert space, then $V_r = BV_r'$ where V_r' is the total inside volume based upon over-all inside dimensions, and B is the fraction of this space available to and occupied by the reacting fluid.

Illustration 7. It is desired to decompose sulfuryl chloride into sulfur dioxide and chlorine in a flow process. From the data of Illustration 4 calculate the reactor volume required to produce 90 per cent decomposition when operating at a constant temperature of 610°F and at atmospheric pressure with a feed rate of 50 lb per hr. It may be assumed that the system follows the ideal-gas law.

Solution: Basis: 100 lb of SO_2Cl_2

From Equation (49),

$$k = k_c/(R'T) = (0.00132)(60)/(0.729)(1070) = (101.5)(10^{-6}) \text{ lb-mole}/(\text{cu ft})(\text{hr})(\text{atm})$$

In Equation (a), Table LIII,

$$n_{A0} = n_0 = 100/135 = 0.741 \text{ lb-mole}; \qquad \omega = \frac{\delta}{n_0} = \frac{1.0}{0.741} = 1.35$$

$$x_A = (0.9)(0.741) = 0.667; \qquad \delta = 1.0; \qquad \omega x_A = 0.9$$

$$1 + \omega n_{A0} = 2.0; \qquad \frac{n_{A0}}{n_{A0} - x_A} = \frac{0.741}{0.741 - 0.667} = 10$$

Substituting,

$$\frac{V_r}{F} = \frac{0.741}{(0.1015)(10^{-3})(1)} [-0.9 + 2.0 \ln 10] = 27{,}100 \text{ (cu ft)(hr)/100 lb}$$

For a plant to process 50 lb per hr of feed, $F = 50$, and

$$V_r = (27{,}100)(0.5) = 13{,}600 \text{ cu ft}$$

This large reactor volume would be required for the uncatalyzed decomposition at this temperature.

Illustration 8. Iodine may be produced by the decomposition of hydrogen iodide according to the following reaction:

$$2\text{HI}(g) \leftrightarrows \text{H}_2(g) + \text{I}_2(g)$$

The reaction velocity constant k_c of the forward reaction at 393°C and 1 atm is given in the International Critical Tables as 0.000588 (22.41 liters)/(g-mole)(min). The corresponding equilibrium constant K_c is 0.0167.

A decomposition process is to be carried out under these conditions in a flow-type reactor with a feed of 2.0 lb-mole of HI per hour. The unconverted hydrogen iodide is separated and recycled. Ideal-gas behavior may be assumed.

Calculate:

(*a*) The percentage decomposition of the HI at equilibrium.

(*b*) The reactor volumes required for conversions of HI equal to 80 per cent and 90 per cent of the equilibrium value.

(*c*) Compare the net production of iodine in pounds per hour per cubic foot of reactor volume for the two cases of part (*b*).

Since this reaction is at constant pressure and does not involve a change in the total number of moles in the system, the design of the flow process is most conveniently handled by means of the integrated equations for constant-volume operations in Table LII. The reactor volume is then obtained from the time of reaction by the relationship $V_r/F = V_f\tau$, where V_r is the reactor volume, F is the feed rate per unit time, and V_f is the specific volume of the reacting mixture.

Basis: 1.0 lb-mole HI

$k_c = 0.000588$

$K_c = 0.0167$

$F = 0.0333$ lb-mole HI per min

x = moles of HI converted

$n_{A0} = 1.0$

$n_A = 1 - x$

$n_{H_2} = n_{I_2} = \dfrac{x}{2}$

(*a*) At equilibrium:

$$K_c = \frac{(n_{H_2})(n_{I_2})}{n_{HI}^2} = \frac{x^2}{4(1 - x)^2} = 0.0167$$

$$x = 0.205$$

(*b*) At 80 per cent of equilibrium conversion, $x = (0.8)(0.205) = 0.164$. This reaction is a reversible second-order reaction of the type represented by Equation (*o*), Table LII.

$$n_{A0} = 1.0; \qquad a = K_c n_{A0}^2 = 0.0167; \qquad c = K_c - \tfrac{1}{4} = -0.2333$$

$n_{R0} = 0$; $b = -2K_c n_{A0} = -0.0334$; $V_f = \frac{T}{273} = \frac{666}{273} = 2.44$ (359 cu ft) per lb-mole

$n_{S0} = 0$; $b^2 = 0.001156$; $V_f^2 = 5.954$

$$q = 4ac - b^2 = 4(0.0167)(-0.2333) - 0.001156 = -0.01674$$

$$\sqrt{-q} = 0.1294$$

From Equation (h), Table LII, if τ is replaced by $\frac{V_r}{FV_f}$

$$\frac{V_r}{F} = \frac{V_f^2 K_c}{k_c} \frac{2.303}{\sqrt{-q}} \log \left[\left(\frac{2cx + b - \sqrt{-q}}{2cx + b + \sqrt{-q}} \right) \left(\frac{b + \sqrt{-q}}{b - \sqrt{-q}} \right) \right]$$

$$\frac{V_r}{F} = \frac{(5.954)(0.0167)}{(0.000588)} \frac{(2.303)}{(0.1294)} \log \left[\left(\frac{2(-0.2333)(0.164) - 0.0334 - 0.1294}{2(-0.2333)(0.164) - 0.0334 + 0.1294} \right) \left(\frac{-0.0334 + 0.1294}{-0.0334 - 0.1294} \right) \right]$$

$$= (3010)(0.86) = 2590 (359 \text{ cu ft})(\text{min})/\text{lb-mole}$$

$$V_r = (2590)(0.0333) = 86.2 (359 \text{ cu ft}) \text{ or } 30{,}900 \text{ cu ft}$$

Similarly, at 90 per cent of equilibrium conversion, $x = 0.185$.

$$V_r = 36{,}500 \text{ cu ft}$$

(*c*) Net rate of production of iodine in pounds per hour per cubic foot:

For 80 per cent conversion $\frac{(2)(126.9)(0.164)}{30{,}900} = 0.00135$ (lb I_2)/(hr)(cu ft)

For 90 per cent conversion $\frac{(2)(126.9)(0.185)}{36{,}500} = 0.00129$ (lb I_2)/(hr)(cu ft)

Space Velocity. It may be noted that all of the equations of Table LIII express extent of conversion as a function of V_r/F, the reactor volume per unit feed rate. A convenient unit for expressing this relationship between feed rate and reactor volume in a flow process is the *space velocity* which is defined as *the volumes of feed, measured at standard conditions, per unit time per unit volume of reactor.* This unit has the dimension of reciprocal time ($1/\tau$) which is commonly expressed in hours.

The space velocity has gained widespread use, because it directly expresses the volumetric feed capacity of a reactor and is independent of all units except time. However, care must be taken that the standard conditions at which the feed is measured are clearly designated. In dealing with liquid-phase reactions the space velocity is commonly based on the volume of the liquid feed measured at 60°F and is designated by the symbol S_l expressed in reciprocal hours. For vapor-phase reactions it is convenient to use the symbol S_v to denote the space velocity in reciprocal hours, based on the feed in the ideal-gaseous state at 32°F and 1 atm. In processes in which the feed enters as a liquid but is vaporized before reaction either method of expression may be used, and care is necessary to avoid confusion.

From the definitions of space velocity it follows that

$$S_l = \left(\frac{F}{V_r}\right) V_f^\circ \tag{86}$$

where V_f° = the volume of a unit mass of feed at the selected standard conditions, expressed in the same units as V_r, the reactor volume.

In dealing with vapor-phase reactions a convenient simplification results if F is expressed in moles per hour and V_r is expressed in normal molal volumes. In these units

$$S_v = \frac{F}{V_r} \tag{87}$$

where

F = feed rate in pound-moles or gram-moles per hour
V_r = reactor volume in 359 cu ft or 22.4 liters

REACTIONS OF COMPLEX ORDER

As is pointed out on page 819, reactions which from their stoichiometric equations might be expected to be of simple order frequently yield rate equations of complex order. Although it is believed that any reaction of complex order can be expressed in terms of a succession of reactions of simple order, the resulting expressions are frequently so complex that it becomes expedient to employ empirical rate equations. Such empirical equations may be used satisfactorily where the reverse reaction is negligible and equilibrium is not a consideration.

An empirical rate equation of complex order for an irreversible reaction is developed from experimental data by graphical differentiation of curves relating conversion to time or volume. The resulting reaction rates are then empirically related to activities or concentrations. Such rate equations may be applied to problems of reactor design by the same procedures used for reactions of simple order.

Where reverse reactions and equilibria are involved, the problem is much more difficult. If it is attempted to develop empirical equations of complex order for both the forward and reverse reactions, their forms must be such as to satisfy the thermodynamic requirements of equilibrium. It is difficult to accomplish this result by a purely empirical procedure, and it is preferable to develop a form of equation based on a simplified sequence of intermediate reactions which can be combined into a consistent over-all equation. Such equations may be classed as semiempirical. They are thermodynamically consistent and may be applied at equilibrium conditions. However, because of the necessary simplifying assumptions as to mechanism they may not be valid over wide ranges of conditions. Where wide ranges of conditions are involved it may be necessary to develop different sets of constants for different ranges. Such difficulties are avoided if fundamentally sound equations can be developed by consideration of the rate-controlling steps of the sequence of reactions actually taking place.

The formation of hydrogen bromide from hydrogen and bromine is a classical example of a reaction of complex order which has been extensively studied[4]. The experimental measurements indicate that the initial rate is proportional to the first power of the hydrogen concentration and to the square root of the bromine concentration. However, a rate equation of this form is not valid except at initial conditions, and as conversion proceeds the rates are much lower than calculated. This indicates the effect of a reverse reaction, even though the over-all thermodynamic equilibrium constant is very large and the reaction should go substantially to completion at the conditions investigated.

Fundamental equations in agreement with this behavior may be developed by consideration of the series of possible reactions given on page 820. The fact that the initial rate is proportional to the square root of the bromine concentration indicates that the bimolecular reaction between bromine and hydrogen (1) is not the predominant mechanism so it will be assumed that this reaction is slow and may be neglected.

The dissociation of hydrogen into atomic hydrogen is accompanied by a large absorption of energy and is known to be slow at low temperatures; accordingly this reaction rate will be neglected. The reaction between hydrogen atoms and bromine atoms should require practically no energy of activation, and its reaction velocity constant should be high. However, the concentrations of both atomic forms should be extremely low, and it will be assumed that the rate of formation of HBr by this reaction is negligible. With these three reactions eliminated, only (2), (4), and (6) remain for consideration.

$$Br_2 \leftrightarrows 2Br \tag{2}$$

$$Br + H_2 \rightleftarrows HBr + H \tag{4}$$

$$H + Br_2 \rightleftarrows HBr + Br \tag{6}$$

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[4] R. N. Pease, "Equilibrium and Kinetics of Gas Reactions," Princeton University Press (1942).

These three reactions constitute a chain in which atomic bromine is consumed in reaction (4) and a corresponding amount is produced in reaction (6). Since there is no net consumption of atomic bromine it is reasonable to assume that equilibrium is maintained in reaction (2). Then, if the chemical symbols are taken as representing concentrations,

$$\mathrm{Br} = \sqrt{K_{c2}\mathrm{Br}_2} \tag{88}$$

where

K_{c2} = the equilibrium constant of reaction (2)

If only reactions (2), (4), and (6) are significant, the rates of (4) and (6) must be equal, and r the over-all rate of formation of HBr is equal to $2r_4$ or $2r_6$, where

r_4 = rate of removal of H_2 by reaction (4)
r_6 = rate of removal of Br_2 by reaction (6)

Treating (4) and (6) as reactions of simple order, gives

$$r_4 = k_{c4}(\mathrm{Br})(\mathrm{H}_2) - k'_{c4}(\mathrm{HBr})(\mathrm{H}) \tag{89}$$

$$r_6 = k_{c6}(\mathrm{H})(\mathrm{Br}_2) - k_{c6}(\mathrm{HBr})(\mathrm{Br}) \tag{90}$$

where k_{c4} and k_{c6} are the forward and k'_{c4} and k'_{c6} the reverse reaction velocity constants of reactions (4) and (6), respectively. Since the two rates are equal, Equations (89) and (90) may be equated and combined with Equation (88).

$$k_{c4}\sqrt{K_{c2}\mathrm{Br}_2}(\mathrm{H}_2) - k'_{c4}(\mathrm{HBr})(\mathrm{H}) = k_{c6}(\mathrm{H})(\mathrm{Br}_2) - k'_{c6}\sqrt{K_{c2}\mathrm{Br}_2}(\mathrm{HBr}) \tag{91}$$

Solving for H yields

$$H = \frac{k_{c4}\sqrt{K_{c2}\mathrm{Br}_2}(\mathrm{H}_2) + k'_{c6}\sqrt{K_{c2}\mathrm{Br}_2}(\mathrm{HBr})}{k'_{c4}(\mathrm{HBr}) + k_{c6}(\mathrm{Br}_2)} \tag{92}$$

Substituting (92) in (89) gives

$$\tfrac{1}{2}r = r_4 = k_{c4}\sqrt{K_{c2}\mathrm{Br}_2}(\mathrm{H}_2) - k'_{c4}(\mathrm{HBr})\left[\frac{k_{c4}\sqrt{K_{c2}\mathrm{Br}_2}(\mathrm{H}_2) + k'_{c6}\sqrt{K_{c2}\mathrm{Br}_2}(\mathrm{HBr})}{k'_{c4}\,(\mathrm{HBr}) + k_{c6}(\mathrm{Br}_2)}\right] \tag{93}$$

where r = the rate of formation of HBr

Equation (93) is in agreement with the experimental data and indicates that formation of HBr can appreciably affect r_4 even though the over-all equilibrium constant K_1 may be very large. This results from the fact that the relative forward and reverse rates of Equation (93) are dependent on the equilibrium constant of reaction (4) which is not necessarily large.

Equation (93) is complicated but with the constants evaluated could be used in graphical-reaction design methods without difficulty. The evaluation of the constants and the deviations of the equation from experimental data are shown in Illustration 10, page 854.

Chain Reactions. The hydrogen bromide reaction is a simple example of a type of chain reaction commonly encountered particularly in the high temperature decomposition of organic compounds and in oxidation reactions of many types. Rice and coworkers[5] have demonstrated the existence of free radicals in many reacting systems and have proposed various reaction mechanisms involving the continuous formation and removal of these substances. Thus, in the high-temperature decomposition of ethane the controlling reaction is believed to be the formation of methyl and ethyl radicals and atomic hydrogen which may then react with each other and with undecomposed ethane as follows:

$$\begin{aligned}
C_2H_6 &\rightleftarrows H + C_2H_5\\
C_2H_6 &\rightleftarrows 2CH_3\\
C_2H_6 + CH_3 &\rightleftarrows CH_4 + C_2H_5\\
C_2H_6 + H &\rightleftarrows C_2H_5 + H_2\\
C_2H_5 &\rightleftarrows C_2H_4 + H\\
H + C_2H_5 &\rightleftarrows C_2H_4 + H_2\\
H + CH_3 &\rightleftarrows CH_4\\
CH_3 + C_2H_5 &\rightleftarrows C_3H_8\\
2C_2H_5 &\rightleftarrows C_4H_{10}
\end{aligned}$$

According to one interpretation of the free-radical theory of chain reactions the concentrations of free radicals in the reacting system reach constant values after an immeasurably short period. The rates of the other reactions and the rates of formation of ultimate products are then dependent on the concentrations of free radicals as well as those of the other reactants.

An alternate approach to the problem is that used in the development of Equation (93) in which the atoms which are responsible for the chain reaction are assumed to exist in an equilibrium concentration which varies as the reaction progresses. This method has the advantage of leading to thermodynamically consistent equations.

It must be recognized that in the present state of knowledge determination of the mechanism of a chain reaction and the development of rate equations from it must be based on extensive experimental data. With such data available the analysis becomes a problem of testing various plausible mechanisms until one is found which is in satisfactory agreement with the data. The selection of probable mechanisms may be effectively guided by the theory of absolute-reaction rates.[1]

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[5] F. O. Rice and K. F. Herzfeld, *J. Am. Chem. Soc.* **56**, 286 (1934).

Convincing proof of the existence of free radicals has been furnished by various experimental methods, and the chain-reaction theory is supported by the action of *inhibitors* which greatly reduce the rate of a reaction even though present in minute amounts. For example, small traces of nitric oxide are found to reduce markedly the rate of decomposition of ethyl ether. According to the chain-reaction theory such an inhibitor functions by reducing the concentration of free radicals in the system. An inhibitor initially present in a reaction may be consumed by irreversible reactions and finally disappear. Such a situation furnishes the explanation of the frequently observed *induction period* during which a reaction proceeds at an abnormally low rate and then abruptly increases to its normal value. Similarly, there is evidence that the rate of chain reactions can be increased by the presence of small amounts of *accelerators* which serve to increase the free-radical concentrations.

Another experimentally observed phenomenon which supports the chain mechanism is the retarding effect of solid surfaces on many normally homogeneous reactions. It is frequently found that the rate of reaction is increased merely by enlarging the reactor with a resultant reduction of solid surface per unit volume. This effect is explained by the adsorption of free radicals on the solid surfaces which reduces the effective free-radical concentration in the homogeneous phase.

INTERPRETATION OF LABORATORY RESULTS

The laboratory and pilot plant data on which reactor designs must be based are in general of three types:

1. Measurements of composition as a function of time in a batch reactor of constant volume at a substantially constant temperature.
2. Measurements of composition as a function of feed rate to a flow reactor of constant volume operated at constant pressure and substantially constant temperature.
3. Measurements of composition as a function of time in a variable-volume batch reactor operated at constant temperature and substantially constant pressure.

The third type of data is much less common than the other two, and the experimental technique is more difficult. A variable-volume reactor generally depends on varying the level of a confining liquid such as a molten metal in order to maintain constant pressure. This method is desirable where the volume of the reacting system is difficult to calculate as when a change of phase accompanies the reaction. It has the advantage of yielding positive rate measurements and at the same time data on the specific volume of the reacting system.

Data of the second type are generally the most dependable and simple to obtain. This method has the advantage of direct applicability to flow-type reactors. Data of the first type at constant volume are satisfactory except where added moles of gas result from the reaction. In such cases the varying pressures make the data difficult to interpret for complex systems.

Simple Reactions. It has been pointed out that the order of a reaction cannot ordinarily be predicted from its stoichiometry but must be determined experimentally from the relationships of reaction rate to pressure and composition. For reactions proceeding at constant temperature this determination can be based upon either differential or integrated rate equations such as appear in Tables LII and LIII. The integrated forms are particularly convenient for the relatively simple types of reactions to which they are applicable.

If data at constant volume and temperature are available the equations of Table LII are used. If one of these equations properly represents the experimental data a plot of τ against the variable expression on the right side of the equation will yield a straight line having a slope equal to $1/k_c$. Equations based on plausible mechanisms are tested in this manner to confirm the mechanism and order of reaction. For flow reactions the same procedure is followed, the equations of Table LIII being used and V_r/F or $1/S_v$ being plotted instead of τ.

In any case it is desirable to secure data for a wide range of concentrations and conversions for positive determination of the proper rate equation. Such data are obtained by varying the initial compositions of reactants and in gaseous systems by operation at different pressures. From determinations of reaction velocity constants at two temperatures in this manner, the entropy and enthalpy of activation are calculated by the method shown in Illustration 2, and the general equation for the reaction velocity constant in terms of temperature is established.

Complex Reactions. Many processes of commercial importance involve simultaneous and consecutive reactions to such an extent that the development of integrated rate equations for the over-all reactions is impracticable. The analysis of data on such processes may be handled by determining differential rates of reaction r by graphical differentiation of curves relating conversions to time for nonflow reactions or to V_r/F for flow reactions. The differential rates of the individual reactions may be determined in this manner from data on the over-all process.

The individual rates are then correlated with the corresponding concentrations or activities to determine the proper rate equations. This procedure is demonstrated in the following illustration:

Illustration 9. Diphenyl is produced by the pyrolytic dehydrogenation of benzene according to the reaction:

$$(1) \qquad 2C_6H_6 \rightleftarrows C_{12}H_{10} + H_2$$

Triphenyl is also formed by the secondary reaction:

$$(2) \qquad C_6H_6 + C_{12}H_{10} \rightleftarrows C_{18}H_{14} + H_2$$

Reliable rate data are not available on these reactions, but the following approximate data, based on estimates prepared by L. S. Kassell, were presented by Murphy, Lamb, and Watson[6].

In a laboratory investigation of the pyrolysis of benzene to diphenyl, liquid benzene is vaporized, heated rapidly to the desired reaction temperature, and fed continuously through a reactor tube which is maintained at constant temperature and pressure. Under experimental conditions no appreciable decomposition occurs in the preheater. The reactor tube is 37.5 in. long and 0.5 in. in diameter. The product is withdrawn continuously from the reactor and cooled rapidly to condense the vapor and to avoid further decomposition, and the liquid product is analyzed for benzene, diphenyl, and higher polybenzenes which are assumed to be triphenyls.

The compositions of the liquid product for different feed rates are tabulated in Table A for experiments run at 1265°F and 1 atm and for one run at 1400°F and 1 atm. From these data it is desired to develop complete reaction-rate equations.

Basis of Interpretation. Reaction rates are expressed in pound-moles per hour per 359 cu ft of reactor volume and feed rates F in pound-moles per hour. On this basis, $F/V_r = S_v$ in accordance with Equation (87). The following symbols are used to denote the compounds involved: B = benzene, C_6H_6; D = diphenyl, $C_{12}H_{10}$; and T = triphenyl, $C_{18}H_{14}$.

$$V_r' = \text{volume of reactor} = \frac{37.5\pi}{(16)(1728)} = 0.004263 \text{ cu ft}$$

Since the density of liquid benzene at 60°F is 879 g per liter, if F' is the feed rate in liters per hour,

$$F = \frac{879F'}{(454)(78)} = 0.0248F' \text{ lb-moles per hr}$$

and

$$S_v = \frac{(0.0248F')(359)}{0.004263} = 2089F' \text{ reciprocal hr}$$

The complete composition of the product from each experimental run is calculated from the stoichiometry of the reactions. A typical calculation based on 100 lb of liquid products, is shown in Table B.

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[6] G. B. Murphy, G. G. Lamb, and K. M. Watson, *Trans. Am. Inst. Chem. Engrs.* **34,** 429 (1938).

TABLE A

Pyrolysis of Benzene at 1 Atm Pressure

F' = feed rate of liquid benzene in liters per hour (measured at 60°F)

Percentage Composition of Liquid Product by Weight

	F'	*Per cent B*	*Per cent D*	*Per cent T*
At 1265°F				
	0.846	83.0	14.6	2.4
	0.423	70.8	22.4	6.8
	0.282	62.5	26.2	11.3
	0.212	56.8	27.8	15.4
	0.141	50.3	29.2	20.5
	0.121	48.6	29.4	22.0
	0.106	47.4	29.4	23.2
	0.0282	44.7	29.4	25.9
	0.0141	44.7	29.4	25.9
At 1400°F				
	2.75	84.3	13.7	2.0

TABLE B

Complete Analysis of Reaction Products

F' = 0.846 liter of liquid benzene per hr

	Benzene	*Diphenyl*	*Triphenyl*	*Hydrogen*	*Total*
Molecular Weight	78.1	154.2	230.3	2.016	
Composition of liquid product per cent by weight	83.0	14.6	2.4	....	100
Pound-moles per 100 lb of liquid product	1.0627	0.0947	0.01042	....	1.16782
Equivalent pound-moles of benzene in feed	1.0627	0.1894	0.03126	....	1.28336
Pound-moles of H_2 formed....	0	0.0947	0.02084	....	0.11554
Pound-moles of product per pound mole of feed........	0.8281	0.0738	0.0081	0.0900	1.000
	n_B	n_D	n_T	n_H	n_t

These calculations are summarized in Table C as the compositions of the products leaving the reactor expressed in moles per mole of feed.

In Fig. 168 values of n_B, n_D, n_T and n_H are plotted against the reciprocal of space velocity. From the slopes of these curves the differential reaction rates and reaction velocity constants at 1265°F are determined by meansof the following rate equations for reactions (1) and (2) in which the fugacity coefficients are assumed to be 1.0 at the low pressure involved:

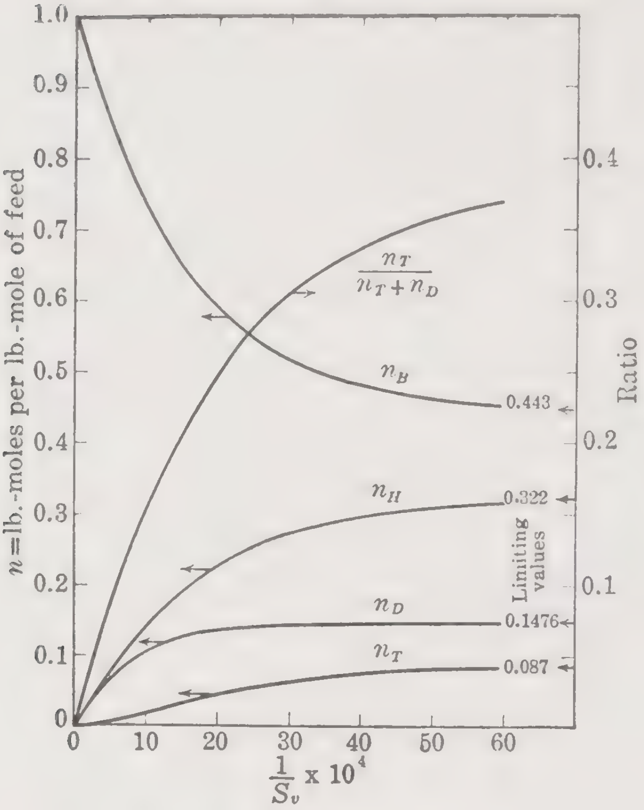

FIG. 168. Pyrolysis of Benzene.

TABLE C

SUMMARY OF COMPOSITIONS OF TOTAL PRODUCTS

F' = feed rate, liters liquid benzene per hour (measured at 60°F)
$S_v = 2089F'$ = gas space velocity at 32°F (1 atm.), in reciprocal hours
$F = 0.0248F'$ = feed rate, pound moles per hour
n = moles per mole of feed

F'	S_v	$1/S_v(10^4)$	n_B	n_D	n_T	n_H	$\frac{n_T}{n_D + n_T}$
At 1265°F							
0.846	1766	5.63	0.828	0.0738	0.00812	0.0900	0.099
0.423	883	11.32	0.704	0.113	0.02297	0.1590	0.169
0.282	588	16.97	0.622	0.1322	0.03815	0.2085	0.224
0.212	442.5	22.62	0.565	0.1400	0.0519	0.2440	0.270
0.141	294.5	34.0	0.499	0.1468	0.0691	0.2847	0.320
0.121	252.7	39.7	0.482	0.1477	0.0740	0.2960	0.337
0.106	221.7	45.2	0.470	0.1477	0.0781	0.3040	0.346
0.0282	58.9	169.7	0.443	0.1476	0.0870	0.3220	0.370
0.0141	29.47	339.3	0.443	0.1476	0.0870	0.3220	0.371

At 1400°F							
2.75	5750		1.735	0.841	0.0695	0.0068	0.0830

$$r_1 = \frac{-dn_{B1}}{d(1/S_v)} = \frac{k_1\pi^2}{n_t^2}\left(n_B^2 - \frac{n_D n_H}{K_1}\right) \tag{a}$$

$$r_2 = -\frac{dn_{D2}}{d(1/S_v)} = \frac{k_2\pi^2}{n_t^2}\left(n_B n_D - \frac{n_T n_H}{K_2}\right) \tag{b}$$

$$-\frac{dn_B}{d(1/S_v)} = r_1 + r_2 \tag{c}$$

$$\frac{dn_D}{d(1/S_v)} = -r_2 + \frac{r_1}{2} \tag{d}$$

$$\frac{dn_T}{d(1/S_v)} = r_2 \tag{e}$$

$$\frac{dn_H}{d(1/S_v)} = \frac{r_1}{2} + r_2 \tag{f}$$

where

r_1, r_2 = rates of reactions (1) and (2), respectively, lb-moles/(hr) (359 cu ft)
k_1, k_2 = reaction velocity constants of reactions (1) and (2), lb-moles/(hr) (atm)^2 (359 cu ft)
S_v = gas space velocity at 32°F and 1 atm (1/hr)
n_B, n_D = moles of benzene and diphenyl, respectively, per mole of feed
n_t = total moles per mole of feed $= n_B + n_D + n_T + n_H$
π = total pressure, atmospheres
K_1, K_2 = equilibrium constants of reactions (1) and (2), respectively

Values of $\dfrac{dn_D}{d(1/S_v)}$ and $\dfrac{dn_T}{d(1/S_v)}$ are obtained by graphical differentiation of the n_B and n_T curves of Fig. 168 at various space velocities. These values are summarized in columns 3 and 4 of Table D.

Values of the equilibrium constants K_1 and K_2 at 1265°F for the two reactions are obtained from the equilibrium compositions approached at low space velocities. Since each reaction proceeds with no change in number of moles, and fugacity coefficients may be neglected at the low pressures employed, the values of K_1 and K_2 may be estimated from the data of Table C at the lowest space velocity.

$$K_1 = \frac{n_D n_H}{n_B^2} = \frac{(0.1476)(0.3220)}{(0.443)^2} = 0.242 \tag{g}$$

$$K_2 = \frac{n_T n_H}{n_B n_D} = \frac{(0.0870)(0.3220)}{(0.443)(0.1476)} = 0.428 \tag{h}$$

The reaction velocity constants k_1 and k_2 may now be obtained from Equations (a) and (b) where n_t the total number of moles of reacting system per mole of feed is constant and equal to 1.0. For example, for a space velocity of 883 reciprocal hr from Equation (a),

$$k_1 = \frac{r_1}{\left[n_B^2 - \dfrac{n_D n_H}{K_1}\right]} = \frac{(146.4)}{\left[(0.704)^2 - \dfrac{(0.113)(0.1590)}{0.242}\right]}$$

$$= 347 \text{ lb-mole/(hr) (359 cu ft) (atm)}^2$$

From Equation (b),

$$k_2 = \frac{r_2}{(n_B n_D) - \left(\dfrac{n_T n_H}{K_2}\right)} = \frac{(28.5)}{\left[(0.704)(0.113) - \dfrac{(0.02297)(0.159)}{0.428}\right]}$$

$$= 400 \text{ (lb-mole)/(hr)(359 cu ft)(atm)}^2$$

TABLE D

SUMMARY OF CALCULATED REACTION RATES AND VELOCITY CONSTANTS

r = lb-mole/(359 cu ft)(hr)
k = lb-moles/(359 cu ft)(hr)(atm)^2

S_v	$1/S_v(10^4)$	$-r_2 + \dfrac{r_1}{2}$	r_2	r_1	k_1	k_2
1766	5.63	100.0	22.1	244.2	370	372
883	11.32	44.70	28.5	146.4	347	400
588	16.97	20.20	26.2	93.6	342	411
442.5	22.62	9.30	22.0	62.60	351	442
294.5	34.0	3.18	10.1	26.36	342	370
252.7	39.7	0.962	8.1	18.12	350	406
221.7	45.2	0	0.6	1.20	338	430
58.9	169.7	0	0	0		
29.47	339.3	0	0	0		
				Average	348	404

The constancy of the reaction velocity constants in Table D confirms the assumption that the reactions are consistently of the second order. A more conclusive test would be to operate the reaction under widely different pressures and redetermine the reaction velocity constants. These constants are unaffected by pressure if the proper rate equations are used and deviations from ideal-gas behavior are considered.

Comparison of the composition of the products in Table C obtained in the single run at 1400°F and a space velocity of 5750 with the curves of Fig. 168 indicates that at 1265°F this same composition is obtained at a space velocity of 1815. Since the conversion is small, this indicates that the rates of the forward reactions are equally accelerated by increase in temperature. With this assumption the rates of the forward reactions at 1400°F are 5750/1815 or 3.16 times faster than at 1265°F. Thus, at 1400°F (1033°K),

$$k_1 = (3.16)(348) = 1100 \text{ lb-moles/(359 cu ft)(hr)(atm)}^2$$
$$k_2 = (3.16)(404) = 1276 \text{ lb-moles/(359 cu ft)(hr)(atm)}^2$$

The enthalpies of activation $\Delta H^\ddagger$, of the two forward reactions are equal with the assumption made and may be calculated from Equation (18). Thus,

$$\log \frac{k_{1033}}{k_{958}} = \frac{-\Delta H^\ddagger}{4.576}\left(\frac{1}{1033} - \frac{1}{958}\right) = \log 3.16$$

$$\Delta H^\ddagger = 30{,}190 \text{ cal per g-mole}$$

Equations for the velocity constants of the forward reactions are completed by evaluating the group of terms $(\mathbf{k}/hR')e^{\Delta S^\ddagger/R}$ of Equation (18). If this group is denoted by A, $k = \dfrac{A}{\nu^{\ddagger} z_m} e^{-\Delta H^{\ddagger}/RT}$ and, if it is assumed that $\nu^{\ddagger} z_m = 1.0$,

$$A_1 = (1100)\left[e^{\frac{30190}{(1.987)(1033)}}\right] = (1100)(2.44)(10)^6 = 2.68(10^9)$$

$$A_2 = (1276)(2.44)(10)^6 = (3.11)(10^9)(\text{lb-mole})/(\text{hr})(359\text{ cu ft})(\text{atm})^2$$

$$k_1\nu^{\ddagger} z_m = (2.68)(10^9)e^{\frac{-30190}{RT}} = (2.68)(10^9)(10)^{\frac{-6597}{T}}$$

$$k_2\nu^{\ddagger} z_m = (3.11)(10^9)(10)^{\frac{-6597}{T}}$$

In order to complete the over-all reaction rate equation it is necessary to evaluate the equilibrium constants as functions of temperature. The best available data for the heat capacities and absolute entropies are used to calculate the standard entropy changes of the reactions and evaluate the constant I_S of Equation (XVI-10). From the experimentally determined equilibrium constants at 1265°F the corresponding values of $\Delta G°/T$ are calculated from Equation (XVI-6) and the constant I_H evaluated from Equation (XVI-11). Thus, complete equations are obtained expressing $\Delta H°$, $\Delta S°$, and $\Delta G°/T$ as functions of temperature which are consistent with the measured equilibrium data.

Reliable data for the entropies of hydrogen and benzene (g) are given in Table XXXV, page 701. The heat-capacity constants for hydrogen are given in Table V, page 214, and those for benzene (g) in Table XXXIX, page 759. These latter values are based directly on the data of Pitzer and Scott from which the entropy in Table XXXV was obtained. The entropies and heat-capacity constants for diphenyl and triphenyl may be estimated from the group contributions of Tables XXXIX–XLIII. The triphenyl is assumed to be a mixture of the ortho, meta and para forms in equal proportions. These results are summarized in Table E.

TABLE E

Thermodynamic Properties

	$\overset{\circ}{S}_{298.2}$	a	$(b)(10^3)$	$(c)(10^6)$
Hydrogen (g)	31.23	6.88	0.066	0.279
Benzene (g)	64.39	0.23	77.83	−27.16
Diphenyl (g)	98.1	−0.20	149.11	−52.25
Triphenyl (g)	128.2	1.74	214.33	−73.65
	$\Delta \overset{\circ}{S}_{298.2}$	Δa	$\Delta b(10^3)$	$\Delta c(10^6)$
Reaction (1) $2B = D + H$	0.55	6.22	−6.48	+2.35
Reaction (2) $B + D = T + H$	−3.06	8.59	−12.54	+6.04

From Equation (XVI-10) and the data of Table E:

Reaction (1), $I_S = 0.55 - (6.22)(\ln 298.2) + (6.48)(298.2)(10^{-3}) - (1.17)(298.2)^2(10^{-6}) = -33.05$

Reaction (2), $I_S = -3.06 - (8.59)(\ln 298.2) + (12.54)(298.2)(10^{-3}) - (3.02)(298.2)^2(10^{-6}) = -48.53$

From Equation (XVI-23) and the experimental equilibrium constants of Equations (g) and (h),

(1) $(\Delta G^\circ/T)_{958} = -4.576 \log 0.242 = 2.82$ cal/(g-mole)(°K)

(2) $(\Delta G^\circ/T)_{958} = -4.576 \log 0.428 = 1.69$ cal/(g-mole)(°K)

From these results the constants I_H in Equation (XVI-11) are evaluated.

(1) $I_H = 958[2.82 - (6.22 + 33.05) + (6.22)(\ln 958) - (3.24)(958)(10^{-3}) + (0.39)(958)^2(10^{-6})] = 3363$ cal per g-mole

(2) $I_H = 958[1.69 - (8.59 + 48.53) + (8.59)(\ln 958) - (6.27)(958)(10^{-3}) + (1.01)(958)^2(10^{-6})] = 1475$ cal per g-mole

The standard heats of reaction at 298°K may be calculated from (XVI-9):

(1) $\Delta H_{298} = 3363 + (6.22)(298.2) - (3.24)(298.2)^2(10^{-3}) + (0.78)(298.2)^3(10^{-6}) = 4950$ cal per g-mole

(2) $I_H = 958[1.69 - (8.59 + 48.53) + (8.59)(\ln 958) - (6.27)(958)(10^{-3}) + (1.01)(958)^2(10^{-6})] = -1475$ cal per g-mole

The available calorimetric data indicate a heat of reaction at 298°K of 7,250 cal per g-mole for reaction (1). This is in poor agreement with the value previously calculated from the estimated entropy change and equilibrium data although the difference is only 0.15 per cent of the heat of combustion of diphenyl. The discrepancy may result from errors in any of the three sets of data involved. Such inconsistencies are constantly encountered in the present state of development of thermodynamic data and must be rationalized as well as possible. In this case the discrepancy in heats of reaction will not seriously affect the equilibrium or kinetic calculations over the temperature range of interest, and the calculated values will be used to maintain consistency with the equilibrium measurements. In the design of the reactor, to which heat must be supplied for the endothermic reaction, the calorimetric heat of reaction may be used to insure a more conservative design.

An alternate procedure would be to accept the calorimetric and estimated heats of reaction at 298°K and the heat-capacity equations and calculate the standard entropy changes from the equilibrium measurements. In general, however, as a result of spectroscopic and statistical methods, absolute entropy data are more reliable than calorimetric heats of reaction.

The equilibrium constants are expressed by the following equations obtained by substituting the calculated values of I_H, I_S, Δa, Δb, and Δc in Equations (XVI-11 and 23).

$$-4.576 \log K_1 = \frac{3363}{T} + 39.27 - (14.32)(\log T) + (3.24)(10^{-3})T - (0.39)(10^{-6})T^2 \quad \text{(i)}$$

$$-4.576 \log K_2 = \frac{-1475}{T} + 57.12 - (19.78)(\log T) + (6.27)(10^{-3})T - (1.01)(10^{-6})T^2 \quad \text{(j)}$$

Reaction rates in lb-moles/(hr)(359 cu ft) are calculated by substituting the foregoing values for the equilibrium constants in the following equations:

$$r_1 = \frac{(2.68)(10)^9\pi^2}{(10)^{\frac{8597}{T}}\nu^{\ddagger}z_m n_t^2}\left[(n_B\nu_B)^2 - \frac{(n_D\nu_D)(n_H\nu_H)}{K_1}\right] \quad \text{(k)}$$

$$r_2 = \frac{(3.11)(10)^9\pi^2}{(10)^{\frac{6597}{T}}\nu^{\ddagger}z_m n_t^2}\left[(n_B\nu_B)(n_D\nu_D) - \frac{(n_T\nu_T)(n_H\nu_H)}{K_2}\right] \qquad (l)$$

where T = temperature, degrees Kelvin
π = total pressure, atmospheres
$\nu^{\ddagger}$ = fugacity coefficient of the activated complex
z_m = compressibility factor of the reaction mixture
n_B, n_D = moles of components $B, D, \ldots$ in a reaction mixture of n_t total moles
ν_B, ν_D = fugacity coefficients of components $B, D, \ldots$

At moderate pressures deviations from ideal behavior may be neglected by assuming that the fugacity coefficients in the numerators of Equations (k) and (l) approximately cancel the products $\nu^{\ddagger}z_m$ in the denominators.

The method of graphical differentiation demonstrated in Illustration 9 is theoretically sound but frequently is difficult to apply satisfactorily to the scattered and erratic data which are typical of kinetic measurements. Small changes in the shape of the curve drawn through such data have relatively large effects on the measured slopes and result in widely varying rates. In such cases it may be necessary to consider the average rates which are evaluated by differentiation as merely first approximations which are adjusted by trial until the conversion curves calculated by their graphical integration show satisfactory agreement with the experimental data. Methods of integration are discussed in the following section on reactor design.

A more direct and accurate method of evaluating velocity constants from complex integral conversion data was pointed out by Reiser and Watson[7] and Myers and Watson[8]. This method is applicable where the number of moles converted per mole of feed by the reaction in question can be established from the disappearance of some reactant or the appearance of a product. Where several simultaneous reactions are involved it may be necessary to evaluate successively the conversions attributable to the individual reactions by a series of material balances, starting with reactions which are solely responsible for the disappearance of some reactant or the appearance of some product. For example, in Table C of Illustration 9, page 848, at a feed rate of 0.0141, there is 0.0870 mole of triphenyl produced which establishes the conversion of reaction (2) as corresponding to 0.0870 mole of benzene. The conversion by reaction (1) is then $1 - 0.443 - 0.0870 = 0.470$ mole of benzene. This same procedure may be followed in more complex systems.

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[7] C. O. Reiser and K. M. Watson, *Natl. Petroleum News*, Tech. Sec. **38**, *R*260 (April 3, 1946). "Principles of Reactor Design," National Petroleum Publishing Company, Cleveland (1946).

[8] P. S. Myers and K. M. Watson, *Natl. Petroleum News*, Tech. Sec. **38**, *R*388 (May 1, 1946), and **38**, *R*439 (June 5, 1946). "Principles of Reactor Design," National Petroleum Publishing Company, Cleveland (1946).

Once the conversion attributable to a reaction is established at several different values of V_r/F for a given feed at constant temperature and pressure, the reaction velocity constant corresponding to each experimental point may be established by graphical integration. Thus, if the reaction is of the first order in the forward direction and of the second order in the reverse direction, the following expression results from combining the basic rate equation with Equation (81) and rearranging:

$$k_1 = \frac{F}{V_r\pi}\int_0^{x_{A_1}} \frac{dx_{A1}}{\dfrac{n_A}{n_t} - \dfrac{n_R n_S \pi}{n_t^2 K}} \tag{94}$$

where

k_1 = reaction velocity constant of reaction (1)
x_{A1} = moles of component A converted *by reaction* (1) per mole of feed
n_A,n_R,n_S = moles of components A, R, and S present in the reacting system per mole of feed
n_t = total moles of reacting system per mole of feed

Each of the quantities in the integral of Equation (94) may be evaluated for each experimental point. A curve is then plotted relating x_{A1} as abscissas to $1/(n_A/n_t - n_R n_S \pi/n_t^2 K)$ as ordinates. The area under this curve between $x_{A1} = 0$ and any selected experimental value of x_{A1} is equal to the product of the reaction velocity constant and the value of $\pi V_r/F$ corresponding to that value of x_{A1}. In this manner a series of values of k_1 is established which may be averaged.

This same method of evaluation may be applied to reactions of higher order, regardless of the complexity of the system if the conversion attributable to the reaction and the numbers of moles of all reactants and products actually present in the system are known for a series of runs at different values of V_r/F on the same feed at a constant temperature and pressure.

Illustration 10. Interpretation of Chain-Reaction Data. In Table A are data on the chain reaction involved in the hydrogenation of bromine gas which have been selected from the experimental work of Bodenstein and Lind.[9] All experiments were conducted at constant volume. An independent analysis of these data is reported by Pease.[10]

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[9] Bodenstein and Lind, *Z. Physik. Chem.*, **57**, 168 (1907).

[10] R. N. Pease, "Equilibrium and Kinetics of Gas Reactions," Princeton University Press (1942).

TABLE A

EXPERIMENTAL DATA OF BODENSTEIN AND LIND ON THE HYDROGENATION OF BROMINE GAS COMPARED WITH CALCULATED RESULTS

Run No.,	I			II			III			IV		
Temp., °K	498.8			524.5			550.6			574.4		
		Calc.	*Exptl.*		*Calc.*	*Exptl.*		*Calc.*	*Exptl.*		*Calc.*	*Exptl.*
	x	τ	τ	x	τ	τ	x	τ	τ	x	τ	τ
	0	0	0	0	0	0	0	0	0	0	0	0
	0 0160	845	840	0.023	165	150	0.0953	130	120	0.0669	15.3	14.5
	0.0273	1485	1500	0.0418	312	300	0.1538	250	240	0.0985	25.1	24.5
	0.0408	2260	2280	0.0831	688	600	0.1936	366	360	0.1262	34.0	34.5
	0.0516	2975	3000	0.1076	952	900	0.2210	482	480	0.1644	50.7	49.5
	0.0635	3765	3720	0.1353	1304	1200	0.2460	627	600	0 2093	79.5	79.5
	0.0732	4473	4500	0.1605	1691	1500	0.2679	868	900	0.2306	98.7	99.5
	0.1025	6703	6600	0.1773	1997	1800	0.2797	1134	1200	0.2502	123.7	124.5
	0.1404	9273	9000	0.2181	3097	2700	0.2852	1370	1440	0.2619	148.3	149.5
				0.2437	4157	3600						

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In each run the initial concentrations a and b expressed in gram-moles per 22.4 liters were as follows:

For H_2, $a = 0.5637$
For Br_2, $b = 0.2947$

In Table A, τ indicates time in minutes and x is the gram-moles of H_2 or Br_2 reacted per 22.4 liters.

The mechanism of this chain reaction is discussed on page 842. In terms of the initial concentrations a and b and the conversion x, Equation (93) may be written to express the reaction rate as follows,

$$\tfrac{1}{2}r = r_4 = r_6 = k_{c4}\sqrt{K_{c2}}\sqrt{b-x}(a-x) - k'_{c4}(2x) \left[\frac{k_{c4}\sqrt{K_{c2}}\sqrt{b-x}(a-x) + k'_{c6}\sqrt{K_{c2}}\sqrt{b-x}(2x)}{k'_{c4}(2x) + k_{c6}(b-x)}\right] \tag{a}$$

The thermodynamic properties of the reactants and products are summarized in Table B, taken from the data of Tables V, XIV, XVII, and XXXV, assuming HBr follows the heat capacity equation of nitrogen.

TABLE B

	$\Delta H^\circ_{f\,291.1}$	$S^\circ_{298.1}$	c°_p
$Br_2(g)$	7650	58.63	$8.58 + (0.30)(10^{-3})T$
$Br(g)$	26,880	41.81	4.97
$H_2(g)$	0	31.23	$6.88 + (0.066)(10^{-3})T + (0.279)(10^{-6})T^2$
$HBr(g)$	−8,650	47.48	$6.30 + (1.819)(10^{-3})T - (0.345)(10^{-6})T^2$
$H(g)$	51,900	27.40	4.97

From these data the thermodynamic changes and equilibrium constants accompanying the individual reaction steps are calculated as follows:

(1) $$H_2(g) + Br_2(g) \rightarrow 2HBr(g)$$

$$\Delta H^\circ_T = -24{,}234 - 2.86T + (1.636)(10^{-3})T^2 - (0.323)(10^{-6})T^3$$
$$\Delta S^\circ_T = 20.462 - 2.86 \ln T + (3.272)(10^{-3})T - (0.485)(10^{-6})T^2$$

		Run I	*Run* II	*Run* III	*Run* IV
T, °K	298.1	498.8	524.5	550.6	574.4
ΔH°	−24,950	−25,244	−25,331	−25,367	−25,399
ΔS°	5.10	4.21	4.13	4.07	4.01
ΔG°		−27,394	−27,498	−27,608	−27,701
K_1		$1.004(10^{12})$	$2.876(10^{11})$	$9.106(10^{10})$	$3.51(10^{10})$
K_{c1}		$1.004(10^{12})$	$2.876(10^{11})$	$9.106(10^{10})$	$3.51(10^{10})$

(2) $$Br_2(g) \rightarrow 2Br(g)$$

$$\Delta H^\circ_T = 45{,}718 + 1.36T - 0.00015T^2$$
$$\Delta S^\circ_T = 17.33 + 1.36 \ln T - 0.0003T$$

		Run I	*Run* II	*Run* III	*Run* IV
T, °K	298.1	498.8	524.5	550.6	574.4
ΔH°	46,110	46,359	46,390	46,421	46,444
ΔS°	24.99	25.63	25.69	25.74	25.799
ΔG°		33,575	32,900	32,249	31,640
K_2		$1.951(10^{-15})$	$1.96(10^{-14})$	$1.579(10^{-13})$	$9.03(10^{-13})$
K_{c2}		$1.068(10^{-15})$	$1.02(10^{-14})$	$7.835(10^{-14})$	$4.29(10^{-13})$

(4) $$H_2 + Br \leftrightarrows HBr + H$$

$$\Delta H_T^\circ = 16{,}471 - 0.58T + 0.876(10^{-3})T^2 - 0.208(10^{-6})T^3$$

$$\Delta S_T^\circ = 1.650 - 0.58 \ln T + 1.753(10^{-3})T - 0.312(10^{-6})T^2$$

		Run I	*Run* II	*Run* III	*Run* IV
T, °K	298.1	498.8	524.5	550.6	574.4
ΔH°	16,370	16,374	16,377	16,382	16,393
ΔS°	1.84	1.84	1.852	1.860	1.863
ΔG°		15,456	15,406	15,358	15,322
K_4		1.692(10⁻⁷)	3.8(10⁻⁷)	8.006(10⁻⁷)	1.512(10⁻⁶)
K_{c4}		1.692(10⁻⁷)	3.8(10⁻⁷)	8.006(10⁻⁷)	1.512(10⁻⁶)

(6) $$H(g) + Br_2(g) \rightarrow HBr(g) + Br(g)$$

$$\Delta H_T^\circ = -40{,}677 - 2.28T + 0.759(10^{-3})T^2 - 0.115(10^{-8})T^3$$

$$\Delta S_T^\circ = 15.813 - 2.28 \ln T + 1.519(10^{-3})T - 0.172(10^{-6})T^2$$

		Run I	*Run* II	*Run* III	*Run* IV
T, °K	298.1	498.8	524.5	550.6	574.4
ΔH°	−41,320	−41,668	−41,709	−41,722	−41,786
ΔS°	3.26	2.36	2.284	2.208	2.15
ΔG°		−42,845	−42,907	−42,938	−43,020
K_6		5.902(10¹⁸)	7.08(10¹⁷)	1.108(10¹⁷)	2.38(10¹⁶)
K_{c6}		5.902(10¹⁸)	7.08(10¹⁷)	1.108(10¹⁷)	2.38(10¹⁶)

With these thermodynamic constants the rate data are analyzed by the following scheme which is demonstrated for Run I at 498.8°K.

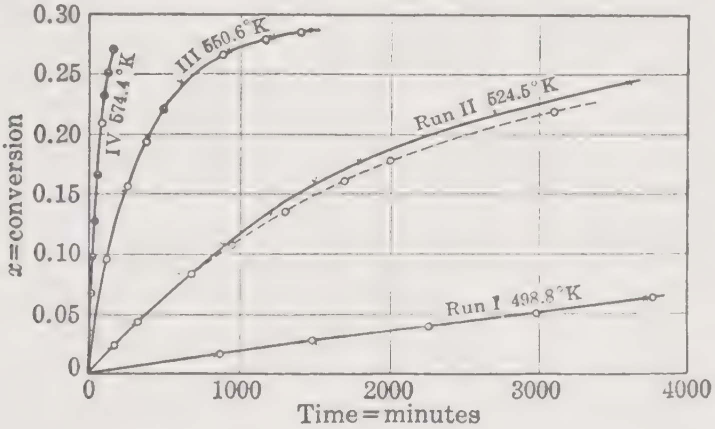

FIG. 169. Hydrogenation of Bromine.

The gram-moles of hydrogen consumed x are plotted against time τ in Fig. 169. From this plot on a large scale values of reaction rates r_4 were obtained by graphical differentiation and plotted on a logarithmic scale against time in Fig. 170. By extension of this plot to $\tau = 0$ the value of $r_4 = k_{c4}\sqrt{K_{c2}}\sqrt{ba} = 1.95(10^{-5})$ is obtained directly, since at zero time the second term of Equation (a) disappears and the value of x is zero. Since K_{c2}, a, and b are known, the value of k_{c4} is obtained.

$$k_{c4} = \frac{1.95(10^{-5})}{(3.27)(10^{-8})(0.542)(0.5637)} = 1.955(10^3)$$

Values of k'_{c4} are calculated from K_{c4}:

$$k'_{c4} = \frac{k_{c4}}{K_{c4}} = \frac{1.955(10^3)}{1.692(10^{-7})} = 1.153(10^{10})$$

Values of k'_{c6} may now be calculated by rearrangement of Equation (a) and the relation $k_{c6}/k'_{c6} = K_{c6}$. Thus:

$$k'_{c6} = \frac{r_4 k'_{c4}(2x)}{k'_{c4}\sqrt{K_{c2}}\sqrt{b-x}(a-x)K_{c6}(b-x) - r_4K_{c6}(b-x) - k_{c4}(2x)^2\sqrt{K_{c2}}\sqrt{b-x}} \qquad \text{(b)}$$

Values of k'_{c6} are calculated from Equation (b) for different times of reaction and tabulated in Table C. It may be observed that there is no definite trend in the calculated values of k'_{c6}. The average value is taken as

$$k'_{c6} = 1.753(10^{-8})$$
$$k_{c6} = k'_{c6}K_{c6} = 1.753(10^{-8})(5.90)(10^{18}) = 1.035(10^{11})$$

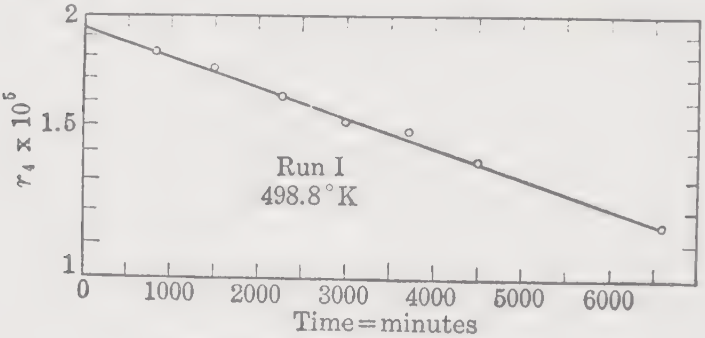

FIG. 170. Evaluation of k_{c4} [Equation (a), Illustration 10].

To test the validity of the equation, the rates of Run I were calculated from Equations (a) and the established constants. The time–conversion relation was then evaluated by graphical integration of the expression

$$\tau = \int_0^x dx/r.$$

The calculated values for Run I are plotted in Fig. 169 and show agreement with experimental data.

In order to establish the validity of Equation (a) at other temperatures, the reaction velocity constants were similarly established for three other runs. The results are summarized in Table D.

In Fig. 171 these reaction velocity constants are plotted on a logarithmic scale against $1/T$. It may be observed that nearly linear plots are obtained with maximum deviations for Run II. From the lines of Fig. 171 values of the enthalpy and entropy of activation of Equation (18) were calculated.

The following results were obtained:

(4)
$$H_2 + Br \rightleftarrows HBr + H$$
$$\Delta H^{\ddagger} = 17{,}720; \qquad \Delta S^{\ddagger} = -9.035$$

TABLE C

Evaluation of k'_{c6} *Run* I 498.8°K (225.7°C)

$$k'_{c6} = \frac{N}{A - B - C}$$

$$N = 2r_4k'_{c4}x$$
$$A = k_{c4}\sqrt{K_{c2}}\sqrt{b - x}(a - x)K_{c6}(b - x)$$
$$B = r_4K_{c6}(b - x)$$
$$C = 4k_{c4}x^2\sqrt{K_{c2}(b - x)}$$

τ	x	$r_4(10^5)$	$N(10^{-3})$	$b - x$	$\sqrt{b - x}$	$(a - x)$	$2x$	$A(10^{-12})$	$B(10^{-12})$	$C(10^{-7})$	$(A-B-C)(10^{-12})$	$k_{c6}(10^8)$
0	0	1.95	0	0.2947	0.542	0.5637	0	33.97	33.92	0	0.05	0
840	0.0160	1.82	6.71	0.2787	0.528	0.5477	0.0320	30.41	29.94	0.1425	0.47	1.427
1500	0.0273	1.74	10.95	0.2674	0.517	0.5364	0.0546	27.98	27.46	0.9853	0.52	2.106
2280	0.0408	1.62	15.24	0.2539	0.504	0.5229	0.0816	25.25	24.28	2.14	0.97	1.571
3000	0.0516	1.52	18.09	0.2431	0.494	0.5121	0.1032	23.20	21.81	3.36	1.39	1.301
3720	0.0635	1.48	21.67	0.2312	0.481	0.5002	0.1270	21.00	20.20	4.96	0.80	2.709
4500	0.0732	1.36	22.96	0.2215	0.471	0.4905	0.1464	19.31	17.77	6.45	1.54	1.491
6600	0.1025	1.115	27.18	0.1922	0.439	0.4612	0.2050	14.68	13.05	11.79	1.63	1.667
9000	0.1404	..	..	0.1543	0.393	0.4233	0.2808	..	..	..	..	..

Average $k'_{c6} = 1.753(10^{-8})$

(6) $$\mathrm{H(g) + Br_2(g) \rightarrow HBr(g) + Br(g)}$$
$$\Delta H^\ddagger = 7200; \qquad \Delta S^\ddagger = 5.24$$

TABLE D

SUMMARY OF REACTION VELOCITY CONSTANTS

	Run I	*Run* II	*Run* III	*Run* IV
T, °K	498.8	524.5	550.6	574.4
k_{c4}	$1.955(10^3)$	$5.77(10^3)$	$1.037(10^4)$	$2.39(10^4)$
k'_{c4}	$1.153(10^{10})$	$1.52(10^{10})$	$1.28(10^{10})$	$1.58(10^{10})$
k_{c6}	$1.035(10^{11})$	$1.035(10^{11})$	$2.29(10^{11})$	$3.106(10^{11})$
k'_{c6}	$1.753(10^{-8})$	$1.46(10^{-7})$	$2.085(10^{-6})$	$1.305(10^{-5})$

From these values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ and the equilibrium constants values of conversion at various times of reaction were calculated for all four runs and plotted in Fig. 169. It may be seen that the calculated values are in close agreement with experimental data for all runs except Run II. It is possible that there was some experimental irregularity in this run.

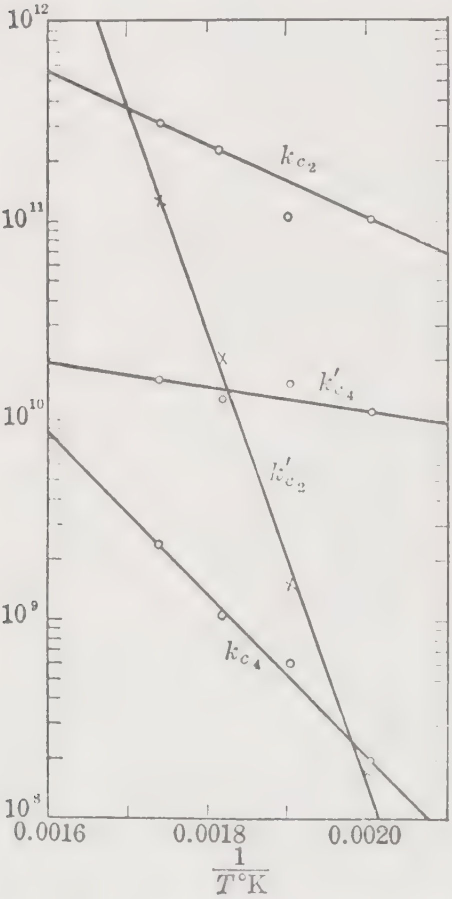

FIG. 171. Effect of Temperature on the HBr Reaction Velocity Constants.

The values of $\Delta H^\ddagger$ calculated by this analysis are in only fair agreement with the experimental and calculated values cited by Glasstone, Laidler, and Eyring for the same reactions.

Product Distribution and Selectivity. In complex systems the over-all effect may be the result of many primary, secondary, and tertiary reactions. Since these individual reactions may exhibit different responses to variations in temperature, pressure, and composition, their combined results frequently present a complex pattern of relationships which can be rationalized only by being resolved into the contributions attributable to individual reaction steps.

In presenting data on such systems it is convenient to designate as *conversion* the decomposition or disappearance of the key or limiting reactant. Thus, *percentage* conversion is the percentage of the key reactant in the feed which is converted into other products. A tabulation of number of moles of each product formed per mole of key reactant decomposed is termed the *product distribution* of the reacting system. The *selectivity* of the reaction is the percentage ratio of the moles of desired product formed per mole of converted key reactant to the number of moles which would have resulted were there no undesired side reactions.

In laboratory studies of such complex systems it is desirable to select a fixed feed composition, temperature, and pressure and to cover wide ranges of conversions by operations at widely different space velocities. The region of low conversions is of importance in identifying the primary reactions, whereas data at high conversions are necessary for the evaluation of secondary reactions.

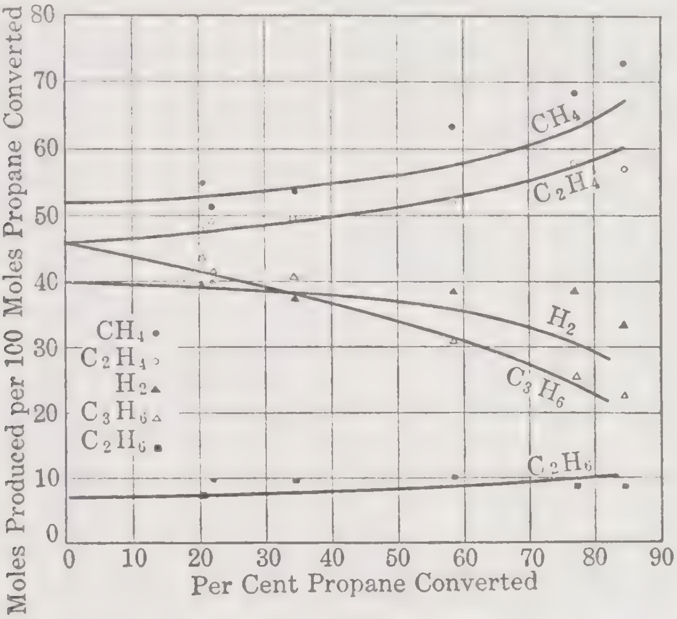

FIG. 172. Distribution of Products from the Pyrolysis of Propane, (at 725°C and 1 atm pressure).

In analyzing such data it is convenient to plot first the complete product distribution of each series of runs as ordinates against percentage conversion. Extrapolation of these curves to zero conversion fixes the product distribution of the primary reactions and gives a basis for identifying these reactions.

In Fig. 172 are the product distribution curves for the pyrolysis of propane at 725°C and 1.0 atm, as plotted by Myers and Watson[8] from the data of Schneider and Frolich.[11] Inspection of these curves shows the primary reaction products to be propylene, hydrogen, ethylene, and methane.

[11] V. Schneider and P. K. Frolich, *Ind. Eng. Chem.*, **23**, 1405 (1931).

This result may be expressed by the following stoichiometric equations:

$$\begin{aligned} C_3H_8 &\rightleftarrows H_2 + C_3H_6 \\ C_3H_8 &\rightleftarrows CH_4 + C_2H_4 \\ 2C_3H_8 &\rightleftarrows C_2H_6 + C_3H_6 + CH_4 \\ 2C_3H_8 &\rightleftarrows C_2H_6 + C_4H_{10} \end{aligned}$$

There is evidence that all of these reactions actually occur through chain-reaction mechanisms involving free radicals of the general type analyzed in Illustration 10. However, in such complex systems this type of fundamental kinetic analysis is difficult, and it is at present more fruitful to adopt a semiempirical approach. Each individual net reaction is assumed to occur in accordance with its simple stoichiometric equation, but with an empirically determined *apparent order of reaction* which is evaluated from the effect of pressure on the rate. Many primary pyrolytic reactions satisfactorily approximate simple first-order results. However, careful analysis[10] of data over wide ranges of conditions indicates that large errors may result from extended extrapolation based on such approximations.

Myers and Watson followed this procedure in analyzing the data from the literature on propane pyrolysis and arrived at the product distribution and rate-of-reaction relationships which are summarized in Table LIV. These reactions are assumed to proceed independently at the indicated rates. However, it should be recognized that these rate equations do not represent truly independent reactions of simple order and that they are reliable only over restricted ranges of conditions in the system for which they were developed.

TABLE LIV

EFFECTIVE OVER-ALL REACTIONS IN PROPANE PYROLYSIS[8]

r = rate of reaction, lb-mole/(cu ft)(hr)
π = total pressure, atm.

$k = Ae^{-\frac{E}{RT}}$; E = cal per g-mole; $K = e^{-\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}}$; T = degrees Kelvin

(1) $C_3H_8 \rightarrow C_2H_4 + CH_4$

$r = k\pi \dfrac{n_{C_3H_8}}{n_t}$; (moles of propane); $A = (3.0158)10^{14}$; $E = 66{,}500$

(2) $2C_3H_8 \rightarrow C_2H_6 + C_3H_6 + CH_4$

$r = k\pi \dfrac{n_{C_3H_8}}{n_t}$; (moles of propane); $A = (3.6745)10^{13}$; $E = 65{,}000$

(3) $C_3H_8 \rightleftarrows C_3H_6 + H_2$

$r = k\pi \left(\dfrac{n_{C_3H_8}}{n_t} - \dfrac{n_{C_3H_6} n_{H_2} \pi}{n_t^2 K}\right)$; (moles of propane)

$A = (9.989)10^{12}$; $E = 60{,}000$; $\Delta H^\circ_{1300^\circ F} = 30{,}505$; $\Delta S^\circ_{1300^\circ F} = 32.85$

(4) $2C_3H_8 \rightleftarrows C_2H_6 + C_4H_{10}$

$$r = k\pi \left[\frac{n_{C_3H_8}}{n_t} - \sqrt{\frac{n_{C_2H_6} n_{C_4H_{10}}}{n_t^2 K}} \right]; \text{ (moles of propane)}$$

$A = (2.490)10^{10}$; $E = 54{,}000$
$K = 1.30$ (substantially independent of temperature)

(5) $C_3H_6 + H_2 \rightarrow CH_4 + C_2H_4$

$$r = k\pi \frac{n_{C_3H_6}}{n_t}; \text{ (moles of propylene)}; \quad A = (5.266)10^7; \quad E = 38{,}000$$

(6) $C_3H_6 \rightarrow 0.149CH_4 + 0.064C_2H_2 + 0.2555C_2H_4 + 0.085C_5H_8 + 0.2555C_4H_8 + 0.0745C_6H_{10} + 0.0745H_2 + 0.053C_2H_6 + 0.053C_4H_6$

$$r = k\pi \frac{n_{C_3H_6}}{n_t}; \text{ (moles of propylene)}; \quad A = (2.746)10^{12}; \quad E = 56{,}000$$

(7) $C_4H_{10} \rightarrow 0.12H_2 + 0.49CH_4 + 0.39C_2H_4 + 0.38C_2H_6 + 0.49C_3H_6 + 0.01C_3H_8 + 0.12C_4H_8$

$$r = k\pi \frac{n_{C_4H_{10}}}{n_t}; \text{ (moles of butane)}; \quad A = (4.78)10^{14}; \quad E = 63{,}000$$

(8) $C_2H_6 \rightleftarrows C_2H_4 + H_2$

$$r = k\pi \left[\frac{n_{C_2H_6}}{n_t} - \frac{n_{C_2H_4} n_{H_2} \pi}{n_t^2 K} \right]; \text{ (moles of ethane)}; \quad A = (9.83)10^{12}; \quad E = 63{,}000$$

$\Delta H^\circ_{1300°F} = 34{,}316$; $\Delta S^\circ_{1300°F} = 32.12$

(9) $C_4H_8 + H_2 \rightarrow CH_4 + C_3H_6$

$$r = k\pi \frac{n_{C_4H_8}}{n_t}; \text{ (moles of butylene)}; \quad A = (4.743)10^{15}; \quad E = 67{,}000$$

(10) $0.287C_2H_2 + 0.333C_6H_{10} + 0.38C_5H_8 \rightarrow 0.472C_6H_6 + 0.91CH_4 + 0.333C_2H_4 + 0.178C$

$$r = k\pi^2 \left(\frac{n_{HHC}^2}{n_t^2} \right); \text{ (moles of total reactants)}; \quad A = (9.34)10^9; \quad E = 35{,}000$$

n_{HHC} = combined moles of reactants

For example, the apparent rate of pyrolysis of butenes as a secondary reaction in the pyrolysis of propane may follow a rate equation which would not be applicable to the pyrolysis of pure butenes. Ultimately it is to be hoped that a practical method can be devised for handling such systems by fundamental reactions involving free radicals similar to those of Illustration 10.

By consideration of the reactions of Table LIV it is possible to predict the conversion and product distribution obtained when propane is pyrolyzed under specified conditions and thus to arrive at optimum procedures. Myers and Watson demonstrated this method by carrying out a design study on a large-scale tubular reactor operating with widely varying temperatures and pressures.

GRAPHICAL REACTOR DESIGN

Industrial reactions are usually complicated either by simultaneous reactions or by varying operating conditions or both. For this reason it is rarely possible to employ integrated rate equations in problems of reactor design. Graphical methods are more generally useful and permit the solution of all types of problems.

Adiabatic Reactors. Large-scale processes are frequently carried out in a flow-reactor system consisting of a preheater in which the charge is heated to the reaction temperature and an adiabatic-reaction chamber which is designed to produce the extent of conversion desired in addition to that obtained in the preheater.

If the flow through a reaction chamber is progressive, without significant turbulence in the direction of flow, the temperature in an endothermic reaction will progressively drop from a maximum at the inlet to a minimum at the outlet. This condition is approached in a reactor having a diameter which is small in comparison to its length. In a reactor having a diameter of the same order as the length of the direction of flow there is opportunity for extreme longitudinal turbulence under certain flow conditions. Such turbulence tends to mix the contents of the reactor to a state of uniform temperature and composition, and the operation becomes both isothermal and adiabatic. Under these conditions the uniform average temperature of the reactor is lower than the temperature of the inlet stream by an amount depending on the endothermic heat of reaction and the conversion produced in the reactor. In effect, the inlet stream is abruptly quenched to a lower uniform temperature upon entering the reactor.

The first condition of progressive temperature change is favored by any factor which diminishes convection, such as small reactor diameter, low heat of reaction, and a small volume change accompanying the reaction. The second condition is formed by all factors which promote convection, such as large diameter of the reactor, high heat of reaction, and a large volume change. This latter condition is approached where an exothermic reaction with a large volume increase is conducted in a vertical reaction chamber with flow in the downward direction. In such a system all changes accompanying the reaction make the mixture less dense which results in extreme turbulence and convection in a downflow system. A similar condition of adiabatic and isothermal reaction is frequently produced by means of mechanical agitation in liquid-phase reactors.

Many reactors operate at conditions intermediate between the two extremes. Since temperature distribution in such reactors is difficult to predict it is desirable to develop a design on both bases and select a conservative intermediate value.

Case 1. *Progressive Changes.* For a simple reaction where the course can be represented by a differential equation involving only one variable conversion term x_A, a direct method of reactor design results from combination of the rate equation with an equation relating temperatures to conversion, such as is developed in Illustration 22 of Chapter VIII, page 309. Such an equation expresses the temperature at any point in an adiabatic reactor as a function of the conversion x_A. Thus:

$$T = f_1(x_A) \tag{95}$$

The rate of the typical reaction, $A + B \rightleftarrows R + S$, is given by Equation (44) in which k and K are functions of temperature represented by Equations (18) and (22), respectively. Thus:

$$k = f_2(T) \tag{96}$$

$$K = f_3(T) \tag{97}$$

By combination of Equations (95), (96), and (97) with the rate equation it is possible to calculate the reaction rate r corresponding to any selected conversion x_A for a particular system at fixed initial conditions. The temperature is first calculated from Equation (95) and the velocity and equilibrium constants from (96) and (97). From a series of such calculations corresponding to different values of x_A a curve may be plotted relating $1/r$ as ordinates to x_A. From Equation (81) it is evident that the area under this curve between x_{A0} and x_A is equal to V_r/F for a flow system. A similar integration for obtaining time of reaction in a batch system is made by plotting $1/rV_c$ against x_A and determining the area under the curve in accordance with Equation (56). Where a large pressure drop occurs through the reactor the general method of integration discussed on page 880 is followed.

Case 2. *Uniform Reactor Conditions.* If conditions of extreme turbulence exist in a reactor the average composition and temperature of the material in the reactor must be the same as those of the product discharged from it. For any selected over-all conversion the outlet temperature is calculated from Equation (95). This temperature fixes the average reaction velocity constant and equilibrium constant for the entire reactor. The average rate of reaction per unit volume of reactor is then calculated directly from Equation (44) the composition of the product being employed. The required reactor volume is then equal to $F(x_A - x_{A0})/r$.

Illustration 11. The decomposition of phosphine is a first-order reaction which proceeds according to the following stoichiometric equation:

$$4PH_3(g) \rightarrow P_4(g) + 6H_2(g) \tag{a}$$

In the International Critical Tables the reaction velocity constant of this reaction is expressed by the following empirical equation with temperature in degrees Kelvin and time in seconds:

$$\log k_c = -\frac{18{,}963}{T} + 2 \log T + 12.130 \tag{b}$$

It is proposed to produce phosphorous by the decomposition of phosphine in an adiabatic-flow reactor. Pure phosphine is fed to the reactor at the rate of 500 lb per hr at atmospheric pressure and at a temperature of 672°C which is the highest temperature permitted by the available materials of construction. The decomposition produced in the preheater and the rate of the reverse reaction may be neglected.

(*a*) Assuming that the reactor is of such shape that the temperature changes progressively without longitudinal turbulence, calculate the reactor volume per pass for various degrees of conversion.

(*b*) Repeat part (*a*) assuming that the adiabatic reactor is of such a shape that the temperature and composition are uniform.

(*c*) For comparison with the results of parts (*a*) and (*b*) plot a curve relating conversion per pass to reactor volume if an isothermal reactor at 672°C is employed.

Solution: (*a*) The standard heat of reaction (a) at 18°C per g-mole of phosphine gas is given by Bichowsky and Rossini[12] as 5665 cal.

The molal heat capacities of phosphine gases were calculated by Hirschfelder[13] from estimated vibration frequencies.

$P_4(g)$; $c_p = 5.9 + 0.0096T$

$PH_3(g)$; $c_p = 6.70 + 0.0063T$

$H_2(g)$; $c_p = 6.88 + 0.066(10^{-3})T + 0.279(10^{-6})T^2$

The following energy balance may be written on the basis of 1 mole of phosphine fed where x is the moles of phosphine decomposed.

$$\int_{291}^{945} (6.70 + 0.0063T)\, dT = 0.25x \int_{291}^{T} (5.9 + 0.0096T)\, dT$$
$$+ 1.5x \int_{291}^{T} [6.88 + 0.066(10^{-3})T + 0.279(10^{-6})T^2]\, dT$$
$$+ (1 - x) \int_{291}^{T} (6.70 + 0.0063T)\, dT + 5665x \tag{c}$$

Upon simplification, this becomes

$$x = \frac{9145 - 6.70T - 0.00315T^2}{5.095T - 0.0019T^2 + 0.14(10^{-6})T^3 + 4341} \tag{d}$$

Solving for x at various values of T yields the following values:

T	x	T	x
945	0	600	0.5917
900	0.0742	500	0.7787
800	0.2432	400	0.9799
700	0.4145		

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[12] "Thermochemistry of Chemical Substances," Reinhold Publishing Company (1936).

[13] J. O. Hirschfelder, private communication (1942).

By plotting T against x, values of T are obtained for regular increments of x. The corresponding values of k_c are calculated from Equation (b).

TABLE A

x	T	k_c(1/hr)	x	T	k_c(1/hr)
0	945	37.19	0.6	596	$2.627(10^{-11})$
0.1	885	1.422	0.7	542	$1.469(10^{-14})$
0.2	826	$3.654(10^{-2})$	0.8	489	$1.913(10^{-18})$
0.3	768	$5.832(10^{-4})$	0.9	440	$3.133(10^{-22})$
0.4	708	$4.603(10^{-6})$	1.0	394	$5.598(10^{-28})$
0.5	652	$1.667(10^{-8})$			

The total pound-moles of product per pound-mole of feed for any degree of conversion x is equal to $(1 + 0.75x_A)$, and the volume v_m of product in cubic feet per pound-mole of feed is given as

$$v_m = (1 + 0.75x_A)\frac{359}{273}T \tag{e}$$

From Equations (47) and (80), $r = \dfrac{F\,dx_A}{dV_r}$

$F = (500)/(34.12) = 14.65$ lb-moles per hr

$$V_r = (14.65)\frac{(359)}{273}\int_0^x \frac{(1 + 0.75x_A)T}{k_c(1 - x_A)}\,dx_A = 19.32\int_0^x f(x)\frac{T}{k_c}\,dx \tag{f}$$

For an adiabatic reactor without longitudinal turbulence, Equation (f) is evaluated from a plot of $\dfrac{19.32Tf(x)}{k}$ against x, as shown in Fig. 173. For selected values of x, values of T and k_c are obtained from Table A, and values of $T\dfrac{f(x)}{k}$ are calculated from Equation (f). The total reactor volume required for a given degree of conversion is obtained by summation of the volumes for small Δx increments from 0 to x. The volume required for any degree of conversion is plotted in Fig. 174.

(b) *Adiabatic Reactor with Uniform Mixing.* If uniform conditions prevail in the reactor because of mixing, the differential form of the rate equation can be used to calculate V_r directly. Thus, from Equation (f) it follows that,

$$V_r = \frac{19.32}{k_c}(T)\left(\frac{1 + 0.75x_A}{1 - x_A}\right)(x_A) \tag{g}$$

Values of T and k_c are obtained from Table A, and the corresponding values of V_r from Equation (g) are plotted in Fig. 174.

(c) *Isothermal Conditions.* Where the reaction proceeds isothermally at 945°K the reaction velocity constant is 37.19 per hr, and Equation (f) may be integrated directly to give

$$V_r = 504[-0.75x - 1.75\ln(1 - x)] \tag{h}$$

In Fig. 174 values of V_r are plotted for various degrees of conversion under the three stated conditions of operation. Comparison of the curves of Fig. 174 shows the excessive size of reactor required for the adiabatic operation of this particular endothermic reaction as compared with constant temperature operation. It is evident that longitudinal mixing in an adiabatic reactor for an endothermic reaction is unfavorable.

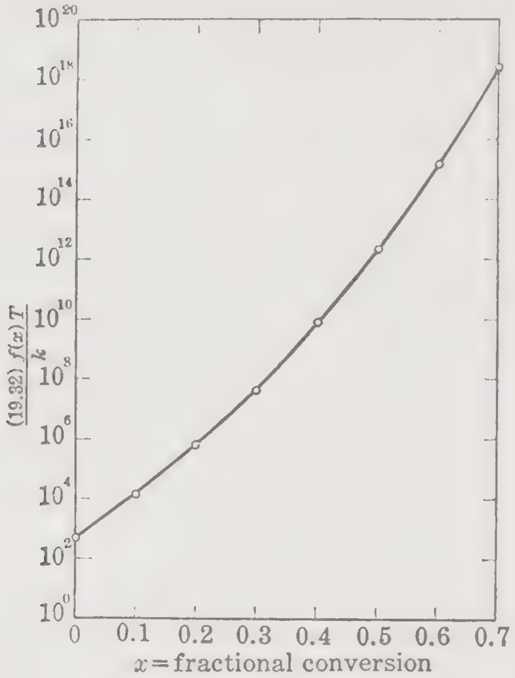

FIG. 173. Integration of Equation (f).

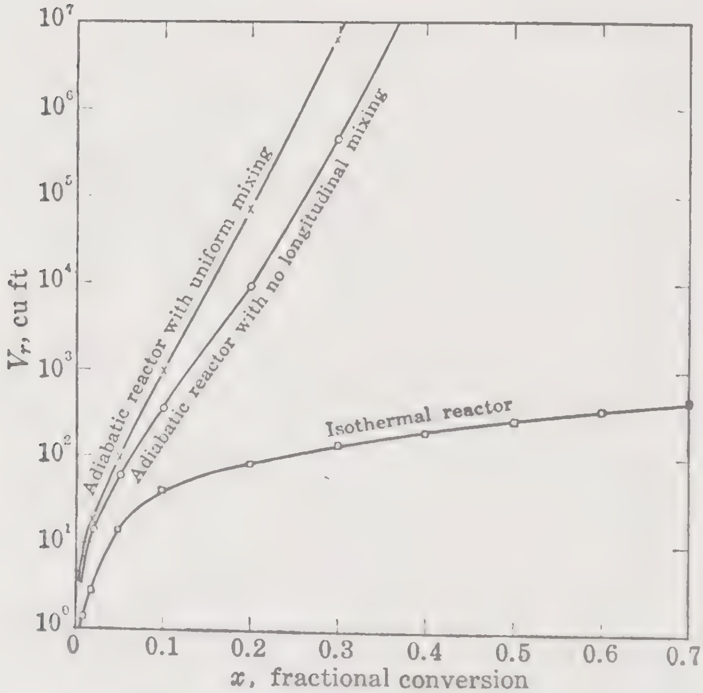

FIG. 174. Volume of Reactor for the Decomposition of Phosphine.

Because of the temperature drop resulting from a highly endothermic reaction it may not be possible to obtain high conversion per pass in an adiabatic reactor of reasonable size. Turbulence or mixing in the reactor is disadvantageous for the endothermic reactions, whereas for most exothermic reactions it is advantageous. In general, adiabatic operation is employed for endothermic reactions where the addition of heat is difficult or where secondary reactions which may accompany high conversion must be avoided. It is sometimes advantageous to add inert components such as nitrogen or steam to increase the heat capacity of the system and thus reduce the temperature drop.

Pressure Drop. The calculation of pressure drops in reactors is frequently a difficult problem, particularly if a change of phase occurs in the reactor. For tubular reactors in which gases are flowing at relatively high velocities pressure drops are satisfactorily represented by the following equation:

$$\frac{dp}{dL} = \frac{0.0235}{D^{4.8}}\left(\frac{w}{1000}\right)^{1.8}\frac{(\mu)^{0.2}}{\rho} \tag{98}$$

where

dp/dL = pressure drop per foot of equivalent pipe length, pounds per (square inch)(ft)

D = internal diameter, inches

w = mass rate of flow, pounds per hour

μ = viscosity, micropoises

ρ = density, pounds per cubic foot

Equation (98) is derived from the general Fanning equation which is treated at length in the standard texts on unit operation and fluid flow. The general equation should be used in dealing with problems involving the flow of liquids or of gases at low velocities.

The problem of pressure drops of gases flowing through beds of granular materials is treated in detail in Chapter XXI, page 1015.

Viscosity. Viscosity is a measure of the resistance to flow offered by a fluid in straight line or laminar motion without turbulence. It may be visualized as resulting from the friction of infinitesimally thin layers of fluid moving over each other. The force required to maintain such relative motion is proportional to the area of contact between the layers and the relative velocity of movement. Thus, viscosity is defined as the force per unit area which is required to maintain a unit velocity gradient, or

$$\mu = F/(A)(du/dx) \tag{99}$$

where

μ = viscosity
F = force in the direction of flow
A = area of surface in relative motion
u = velocity of flow
x = distance, perpendicular to the direction of flow
(du/dx) = velocity gradient

If consistent units are employed, it is evident that viscosity has the dimensions of (force)(time)/(length)^2. In metric units the unit of viscosity is termed the *poise* which is 1.0 (dyne)(sec)/sq cm. The English unit of viscosity is the (poundal)(sec)/sq ft, or, since force equals mass times acceleration, lb/(ft)(sec).

$$1.0 \text{ poise} = 0.0672 \text{ (poundal)(sec)/sq ft or lb/(ft)(sec)}$$

The most commonly used units of viscosity are the *centipoise* which is 0.01 poise and the micropoise which is 10^{-6} poise. The viscosity of water at 68°F is 1.0 centipoise. For this reason viscosities in centipoises are frequently referred to as *viscosities relative to water*.

Kinematic viscosity is defined as the absolute viscosity divided by the density. In the metric system the unit of kinematic viscosity is the *stoke* which has the dimensions of (dyne)(sec)(cm)/g or (sq cm)/sec. The *centistoke* is 0.01 stoke.

Numerical values of viscosities vary over wide range, depending on the nature of the substance and its temperature and pressure. Experimental measurements of viscosity are presented for many substances in the standard tables of physical data. For the most part such data are restricted to pure substances at temperatures near atmospheric and to moderate pressures. Where viscosities must be known at high temperatures or pressures or for fluid mixtures it is frequently necessary to resort to generalized methods of approximation which should be rationalized with whatever direct data are available.

A universal viscosity correlation based on the theorem of corresponding states was proposed by Uyehara and Watson[14] who developed the graphical relationship between reduced viscosity ($\mu_r = \mu/\mu_c$) and reduced temperature and pressure shown in Fig. 175. This relationship is based on consideration of all available data on the variation of viscosity with temperature and pressure in both the liquid and gaseous states. It is approximately the same for all substances.

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[14] O. A. Uyehara and K. M. Watson, *Natl. Petroleum News*, Tech. Sec., **36**, *R*764 (October 4, 1944). Also, "Process Engineering Data," National Petroleum Publishing Company, Cleveland (1944).

By means of Fig. 175 the viscosity of a substance at the critical point μ_c may be estimated from a single viscosity measurement on either the liquid or the gas at any known reduced temperature and pressure. The viscosity at any other temperature and pressure may then be calculated from the equation:

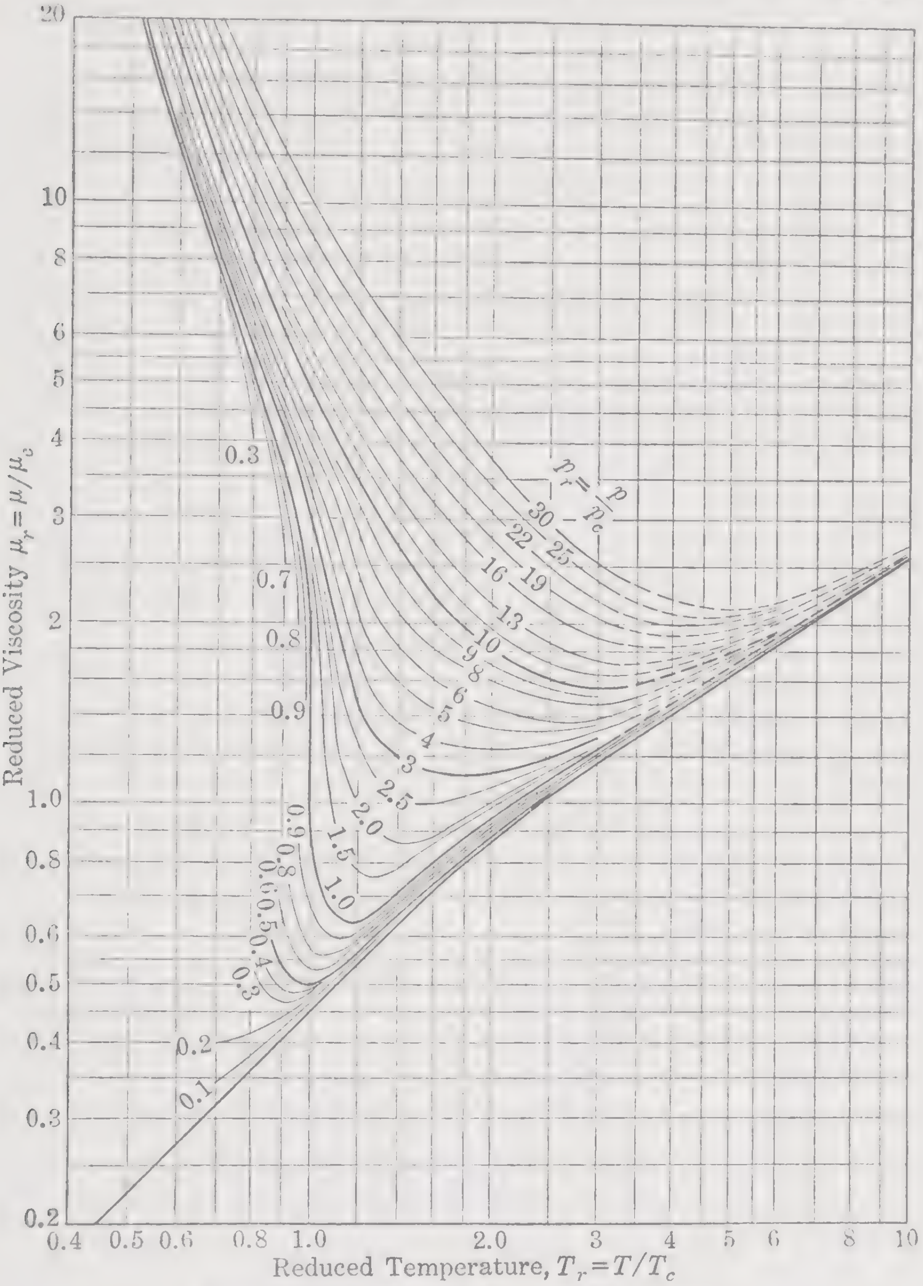

FIG. 175. Generalized Reduced Viscosities.
(Reproduced in "C.P.P. Charts")

$$\mu = \mu_r \mu_c \tag{100}$$

where

μ_r = reduced viscosity read from Fig. 175

μ_c = viscosity at the critical point

In using Fig. 175 in conjunction with experimental viscosity data it is desirable to calculate the value of μ_c used in Equation (100) from data at conditions as close as possible to the range of interest. Thus, although it is possible to estimate the viscosity of a gas from a measurement on the liquid, more reliable results are obtained if calculations for the gas phase are based on gas-phase data wherever possible. The critical viscosities of various substances based on experimental data for the indicated phase are summarized in Table LV.

If no direct viscosity data are available, useful approximations may be calculated from the liquid density or structural parachor together with molecular weight and critical temperature by the following equation:[14].

$$\mu_c = 61.6\,\frac{\sqrt{MT_c}}{(v_c)^{\frac{2}{3}}} = 7.70\,\frac{\sqrt{MT_c}}{(v_1\omega_1)^{\frac{2}{3}}} = 7.70\,\frac{\sqrt{T_c}(\rho_1/\omega_1)^{\frac{2}{3}}}{(M)^{\frac{1}{6}}} \qquad (101)$$

where μ_c = critical viscosity in micropoises

M = molecular weight

T_c = critical temperature, degrees Kelvin

v_c = critical volume, cubic centimeters per gram-mole

$(v_1\omega_1)$ = product of expansion factor (Fig. 109) and molal volume, cubic centimeters per gram-mole

(ρ_1/ω_1) = liquid density in grams per cubic centimeter divided by the expansion factor

A similar expression, based on a knowledge of molecular weight, critical temperature, and critical pressure was derived from an equation proposed by Licht and Stechert.[15]

$$\mu_c = 7.70\,\frac{\sqrt{M}(p_c)^{\frac{2}{3}}}{T_c^{\frac{1}{6}}} \qquad (102)$$

Uyehara and Watson found both Equations (101) and (102) to be in good agreement with over 50 compounds on which data are available. In general the errors were less than 10 per cent. Exceptions are water, hydrogen, helium, and bromine. Equation (101) was found to be more reliable for complex molecules for which good liquid-density data are available, whereas Equation (102) gives better results for the light gases.

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[15] W. Licht, Jr., and D. G. Stechert, *J. Phys. Chem.*, **48**, 23–47 (1944).

TABLE LV

CRITICAL VISCOSITIES

μ_c = *micropoises*

	Phase	μ_c
Acetic acid	g	376
Acetone	g	285
Acetylene	g	237
Air	g	193
Ammonia	g	309
Argon	g	264
Benzene	g	312
n-Butane	g	239
Carbon dioxide	g	343
Carbon disulfide	g	404
Carbon monoxide	g	190
Carbon tetrachloride	g	413
Chlorine	g	420
Chloroform	g	410
Cyclohexane	g	284
Diethylamine	g	276
Ethane	g	210
Ethyl acetate	g	299
Ethyl alcohol	g	334
Ethyl chloride	g	345
Ethyl ether	g	268
Ethyl formate	g	282
Ethyl propionate	g	284
Ethylene	g	215
Helium	g	25.4
n-Heptane	l	254
n-Hexane	g	248
Hydrogen	g	34.7
Hydrogen chloride	g	353
Hydrogen cyanide	g	316
Iso-Butane	g	239
Iso-Butene	g	250
Iso-butyl alcohol	l	319
Iso-butyl formate	g	310
Iso-pentane	g	240
Iso-propyl alcohol	g	297
Krypton	g	396
Methane	g	159
Methyl acetate	g	307
Methyl alcohol	g	375
Methyl chloride	g	338
Methyl propionate	g	301
Naphthalene	l	340
Neon	g	156
Nitric oxide	g	258
Nitrogen	g	180
Nitrous oxide	g	332
n-Nonane	l	265
n-Octane	l	259
Oxygen	g	250
n-Pentane	g	238
Phosphine	g	274
Propane	g	228
Propyl alcohol	g	298
Propyl formate	g	296
Propylene	g	233
Sulfur dioxide	g	411
Toluene	g	306
Water	g	495
Xenon	g	490

Illustration 12. Estimate the viscosity of toluene vapors at a temperature of 700°F and a pressure of 400 lb per sq in. from the following data:

$$T_c = 320.6°\text{C} \qquad p_c = 41.6 \text{ atm}$$

$$\text{At } 20°\text{C}, \quad \rho = 0.866 \text{ g per cc} \qquad M = 92$$

Solution:

$$T_r = (293.2)/(593.8) = 0.494$$

From Equation (XII-40),

$$\omega_1 = 0.1745 - (0.0838)(0.494) = 0.1331$$

$$\rho_1/\omega_1 = (0.866)/(0.1331) = 6.506$$

From Equation (101),

$$\mu_c = 7.70 \frac{(593.8)^{\frac{1}{2}}(6.506)^{\frac{2}{3}}}{(92)^{\frac{1}{6}}} = 310$$

From Equation (102),

$$\mu_c = 7.70 \frac{(92)^{\frac{1}{2}}(41.6)^{\frac{2}{3}}}{(593.8)^{\frac{1}{6}}} = 306$$

At 700°F and 400 lb per sq in.,

$$T_r = (1160)/(593.8)(1.8) = 1.085; \quad p_r = (400)/(41.6)(14.7) = 0.654$$

From Fig. 175, $\mu_r = 0.54$.

From Equation (100),

$$\mu = (0.54)(310) = 168 \text{ micropoises}$$

Viscosities of Mixtures. No entirely satisfactory method is available for estimating the viscosities of mixtures. Uyehara and Watson recommend the assumption that Fig. 175 is applicable to mixtures if the reduced values are based on pseudocritical properties. The pseudocritical viscosity, pressure, and temperature are each taken as equal to the molal average of the true critical properties of the components of the mixture. Thus

$$\mu_c' = N_1\mu_{c1} + N_2\mu_{c2} + N_3\mu_{c3} + \cdots \tag{103}$$

where

μ_c' = the pseudocritical viscosity of a mixture containing N_1 mole fraction of component 1 whose critical viscosity is μ_{c1}, etc.

From the pseudocritical viscosity calculated from Equation (103) the viscosity at any selected pseudoreduced conditions is obtained as the product of μ_c' times the pseudoreduced viscosity μ_r' read from Fig. 175. This method shows fair agreement with data on the viscosity of gaseous mixtures and is believed to be more simple and reliable than methods involving the viscosities of the pure components at the conditions of the mixture.

Nonadiabatic Reactors. In the general case of a process which involves a combination of consecutive and simultaneous reactions, a differential equation may be written for the net rate of disappearance or formation of any reactant or product. This procedure is demonstrated in the development of Equations (a–f) of Illustration 9, page 849 for the production of diphenyl from benzene.

By means of such differential rate equations the over-all results of an operation producing finite changes may be calculated by a stepwise summation of the changes produced in successive small increments of time or reactor volume, starting from the conditions of the original charge. If the incremental steps are small, it may be assumed that the average velocity constants, volumes, and numbers of moles for an increment are the arithmetic means of its terminal values. This method of integration is not unduly tedious and has the advantage of applicability to the most complex systems under conditions of varying temperature, volume, and pressure. Equations similar to (a–f) of Illustration (9) can be written for any combination of reactions.

The summation procedure is best understood by study of Illustration 13 which is a problem in the design of a reactor for a compex system in which temperature and pressure vary simultaneously over wide ranges. The illustration deals with a flow system, but a similar procedure is applicable to batch reactors.

Illustration 13. On the basis of the fundamental data developed in Illustration 9, it is proposed to design a plant for the production of diphenyl by the continuous pyrolysis of benzene in a flow system. A preheater and reactor is desired to produce 35,000 lb per operating day of a mixture of diphenyl and triphenyl containing approximately 30 per cent by weight of triphenyl. The benzene is to be supplied from a vaporizer coil at 700°F. It may be assumed that no conversion takes place in the vaporizer. A trial design is to be based on the use of alloy steel tubes having an inside diameter of 2.0 in. for both the preheater and reactor. The tube materials limit the safe operating temperature of the reactor to a maximum of 1250°F. To obtain maximum capacity per unit volume of reactor the feed will be heated to a temperature of 1250°F and held constant at this temperature in a sufficient number of tubes to produce the desired conversion. A constant heat input rate of 10,000 Btu per hr per sq ft of inside tube surface will be assumed for the preheating section, and the reactor section will be placed in a separate zone in which the heat input may be controlled as necessary to maintain a constant temperature. In order to minimize tar formation the gauge pressure at the reactor outlet will be controlled at 15 lb per sq in.

Calculate the number of tubes 10 ft in length which are required for the preheater and reactor sections, and determine the distribution of temperature, pressure, and composition throughout. The tubes will be connected in series with 180° bends each of which produces a pressure drop equivalent to a length of 50 diameters of straight pipe. The volume of one tube and its return bend is 0.23 cu ft, and the heated length of each tube is 9.2 ft.

The physical data in Table A for the components are taken from the International Critical Tables.

TABLE A

	Benzene	*Diphenyl*	*Diphenyl Benzene*	*Hydrogen*
M	78	154	230	2.0
t_B°C	80.2	255	427	−252.7
t_c°C	288.5	..	..	−239.9
p_c atm	47.7	..	..	12.8
μ (gas) at (t°C) micropoise	123(212.5°C)	..	..	88.2(23°C)

Solution: The specifications of the problems fix the temperature and pressure at the outlet of the reactor and the temperature and conversion at the inlet of the preheater. The inlet pressure is unknown. Since the enthalpies of activation of the forward reactions are approximately equal, and there is no change in the number of moles in either reaction, the distribution of the products is little affected by changes in either reaction temperature or pressure. For this reason the conversion at the reactor outlet may be closely approximated from the specification of the ratio of diphenyl to triphenyl in the product.

A design of this type requires a trial-and-error procedure in which the graphical integration may be started from either end of the reactor. Thus, a first approximation to the inlet pressure may be assumed, and temperature, pressure, and conversion through the preheater and reactor may be evaluated on this basis. If the calculated outlet pressure, corresponding to the desired conversion, does not agree with the specified value, the integration must be repeated with a new trial inlet pressure. Two or three trials of this type generally serve to establish the correct conditions throughout.

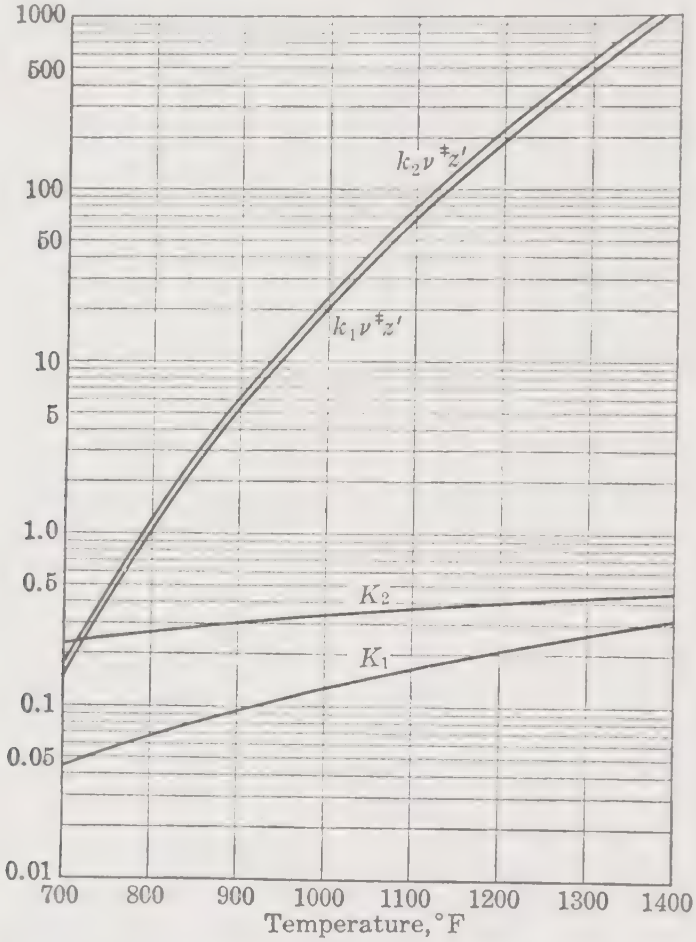

Fig. 176. Reaction Velocity and Equilibrium Constants of the Diphenyl Reaction.

An alternate procedure is to start the integration from the outlet of the reactor and integrate back toward the inlet. In this method it is necessary to assume a trial value of the conversion at the outlet of the preheater. On this basis the conversion, temperature, and pressure throughout the preheater are calculated. If the calculated conversion at the inlet of the preheater does not agree with the specified value, the calculation must be repeated with an adjusted trial value of the conversion at the outlet of the preheater.

The choice between these two procedures is determined largely by personal preference and the conditions of a particular problem. If pressure drop is relatively small and unimportant, the first procedure based on an assumed inlet pressure is generally more convenient. If pressure drop is of considerable importance, and relatively little conversion occurs in the preheater the second alternate is desirable. In questionable cases a combined method may be used in which the first trial integration is carried back from the outlet and a trial inlet pressure is calculated. The second integration may then be carried out in the forward direction, starting with an inlet pressure based on the first calculation. Such a combined procedure will be followed in this illustration.

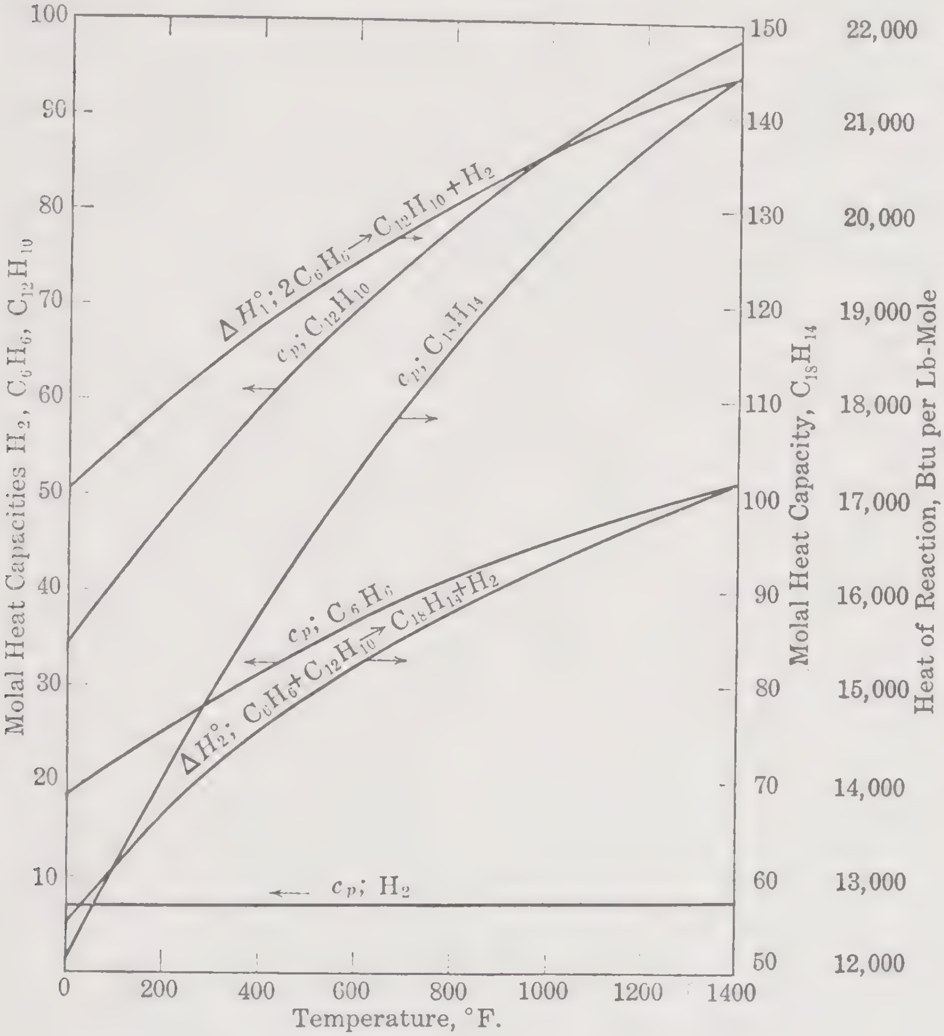

FIG. 177. Thermal Properties of the Diphenyl System.

In carrying out the integrations of a complex problem of this type, values of reaction velocity constants, equilibrium constants, heat capacities, and heat of reaction are required at many different temperatures. Curves expressing these properties as functions of temperature are plotted in Figs. 176 and 177 based on the data of Illustration 9. In order to insure a conservative reactor design the heats of reaction are based on the values calculated from the group contributions of Tables XXXIX–XLIII rather than on the lower values indicated by the equilibrium data.

On this basis:

$$(\Delta H_1)_{298} = 9{,}700; \qquad I_{H1} = 8{,}113 \text{ cal per g-mole of diphenyl}$$
$$(\Delta H_2)_{298} = 7{,}200; \qquad I_{H2} = 5{,}143 \text{ cal per g-mole of triphenyl}$$

In the absence of experimental data the critical temperature and pressures of diphenyl and triphenyl are estimated from the boiling points by means of Equations (III-9, 13, 15), page 71. The critical viscosities of hydrogen and benzene are estimated from the data of Table A and Fig. 175, while the critical viscosities of diphenyl and triphenyl are calculated from Equation (101). These results, together with the available experimental data, are summarized in Table B.

TABLE B

SUMMARY OF CRITICAL PROPERTIES

	Benzene	*Diphenyl*	*Triphenyl*	*Hydrogen*
T_c°R	1011	1458	1895	59.9
p_c lb per sq in.	701	461	385	188
μ_c micropoise	324	317	326	35

SPECIFIED COMPOSITION OF PRODUCT

	Weight Per Cent	*Mole Per Cent*
Diphenyl	70	77.70
Triphenyl	30	22.30

From Fig. 168 may be read the complete composition of the reacting system corresponding to this product composition if the reaction proceeded isothermally at 1265°F. In the plant the average reaction temperature will be lower than 1250°F which will slightly increase the proportion of triphenyl formed with a given conversion of benzene. This qualitative trend results from the fact that, although the enthalpies of activation of the two forward reactions are taken as equal, the equilibrium constant of the first reaction is increased more by an increase in temperature than is that of the second reaction. Accordingly, increased temperature favors the first reaction, and the design will be based on a conversion of benzene slightly lower than that corresponding to the desired product composition at 1265°F. This is accomplished by assuming 12.8 per cent diphenyl in the reactor-outlet mixture instead of the 13.2 per cent indicated by Fig. 168. The proportions of the other components are adjusted to conform to the specified product composition and the stoichiometry of the reactions. Thus, $n_H = 2n_T + n_D$.

Weight of product, lb per hr = 35,000/24 = 1,458
Weight of reactor feed, lb per hr = (1458)/(0.2526 + 0.1086) = 4,036
Molal reactor feed rate F lb-moles per hr = 4036/78.1 = 51.68

It is convenient to consider integral numbers of tubes in carrying out the reactor

REACTOR OUTLET COMPOSITION FOR SPECIFIED PRODUCT COMPOSITION

	At 1265°F from Fig. 168	*Design Basis*	
	Mole Per Cent	*Mole Per Cent*	*Weight Per Cent*
Benzene	62.2	63.36	63.36
Diphenyl	13.2	12.80	25.26
Triphenyl	3.8	3.68	10.86
Hydrogen	20.8	20.16	0.52
	100.0	100.0	100.0

design. In these calculations expressions for the values of Δp, ΔV_r, $\Delta(1/S_v)$ and ΔA, the heated surface area, per tube are required.

Equivalent length of tube, feet, $= 10 + (50)(2)/12 = 18.33$. From Equation (98),

$$\Delta p\text{, lb per sq in., per tube} = \frac{(18.33)(0.0235)(4.036)^{1.8}(359)(z'T)(\mu')^{0.2}(14.7)}{2^{4.8}(78.1)(492)(p)}$$

$$= \frac{0.0262z'T(\mu')^{0.2}}{p} \tag{a}$$

where

z' = mean compressibility factor
T = absolute temperature, degrees Rankine
p = absolute pressure, pounds per square inch
μ' = mean viscosity, micropoises

$$\Delta V_r\text{, (359 cu ft) per tube} = 0.23/359 = 0.641(10^{-3})$$
$$\Delta(1/S_v)\text{ per tube} = \Delta V_r/F = (0.641)(10^{-3})/(51.68) = 0.124(10^{-4})$$
$$\Delta A\text{ sq ft, per tube} = (9.2)(2\pi)/(12) = 4.82$$

The calculations for the first trial analysis of the reactor and the preheater, working back from the reactor outlet, are summarized in Table C. In order to develop a basis for estimating the changes in conditions per tube, the first reaction section considered comprises only the outlet tube. In this analysis the tubes are numbered back from the outlet.

In lines 5–10 are entered the specified reactor-outlet conditions based on 1.0 lb-mole of feed while in lines 11–16 are estimated average conditions in the section. The average composition is arrived at by first estimating average values of n_D and n_T. Then $n_H = 2n_T + n_D$, and n_B is determined by difference.

On the basis of the estimated average composition, the pseudocritical temperature, pressure, and viscosity and the corresponding pseudoreduced temperature and pressure are calculated. Values of the compressibility factor, z', $(c_p' - c_p^*)$, and μ' are read from Figs. 103, 108, and 175. Ideal molal heat capacities and heats of reaction at the average temperature of the section are obtained from Fig. 177. Heat-capacity values are not required in the reactor section where there is no change in temperature.

Values of $k\nu^{\ddagger}z'$ and K are read from Fig. 176. At the moderate pressures of this process the fugacity coefficients of both the activated complex and the reactants and products may be neglected. On this basis the reaction rates are calculated from the following equations:

$$r_1 = \frac{k_1\nu^{\ddagger}z'(\pi)^2}{z'}\left[(n_B)^2 - \frac{n_D n_H}{K_1}\right] \tag{b}$$

$$r_2 = \frac{k_2\nu^{\ddagger}z'(\pi)^2}{z'}\left[n_B n_D - \frac{n_T n_H}{K_2}\right] \tag{c}$$

Thus, in the first section,

$$r_1 = \frac{(300)(32)^2}{(14.7)^2}\left[(0.64)^2 - \frac{(0.1260)(0.1980)}{0.23}\right] = 427$$

Then, since from Equation (87),

$$\Delta(1/S_v) = (\Delta V_r)/(F)$$

$$\Delta n_B = -[(r_1 + r_2)][\Delta(1/S_v)] \tag{d}$$

$$\Delta n_D = [r_1/2 - r_2][\Delta(1/S_v)] \tag{e}$$

$$\Delta n_T = r_2\Delta(1/S_v) \tag{f}$$

$$\Delta n_H = [(r_1/2) + r_2][\Delta(1/S_v)] \tag{g}$$

The incremental conversions calculated from these equations are subtracted from the corresponding numbers of moles at the outlet of the section in order to obtain the compositions at the inlet, which are entered in the next column as the outlet conditions of the next section. The estimated average conditions of the section are compared with these inlet and outlet values, and if any of the estimated values are badly in error the calculation is repeated.

The heat of reaction per mole of feed of each of the reactions is calculated in lines 44 and 45. In the reactor section where there is no change in temperature the sum of these heats of reaction times F the molal feed rate equals q the heat absorbed per hour in the section. Where there is a temperature change,

$$q = F[(\Delta H_1)(\tfrac{1}{2})(-\Delta n_B - \Delta n_T) + (\Delta H_2)(\Delta n_T) - c_p'\Delta T] \tag{h}$$

The temperature change corresponding to a specified heat-input rate is calculated by rearranging equation (h).

$$\Delta T = \frac{q/F - (\Delta H_1)(\tfrac{1}{2})(-\Delta n_B - \Delta n_T) + (\Delta H_2)(\Delta n_T)}{c_p'} \tag{i}$$

The pressure drop in the section is calculated from Equation (a). Thus, for the first section,

$$\Delta p = \frac{(0.0262)(1710)}{32}(208)^{0.2} = 4.1$$

Based on the conversion and pressure drop in the first tube, the average conditions in the section comprising the next five tubes are estimated, it being remembered that the rate of conversion is markedly affected by the increase in pressure. The conversion and pressure drop in these tubes are then calculated, and the same procedure is repeated for another section of five tubes.

It may be noted that in the first 11 tubes of the reactor the mole fraction of benzene is increased from 0.63 to 0.86. Since the reaction rates are high in tubes 7–11 it is evident that another section of five tubes at the constant temperature of 1250°F would account for substantially all of the desired conversion, leaving none to be accomplished in the preheater. Accordingly, it will be assumed that tube 11 is the last tube of the reactor section and that following tubes are heated at a uniform rate of 10,000 Btu/(sq ft)(hr). On this basis calculations are carried out for tube 12 and then for the section comprising tubes 13–15. The results of these calculations are summarized as they are carried out in Fig. 178 in which conditions at the tube outlets are plotted against tube numbers. The curves representing these first calculations for tubes 12–15 are shown by broken lines. It may be noted that these broken lines for the moles of diphenyl and triphenyl are rapidly approaching zero at temperatures far above the specified temperature at the inlet to the preheater. This situation indicates that the number of tubes assumed for the reactor section is too large.

As a second approximation, it is assumed that only six tubes are required for the reactor section. On this basis the changes in tubes 7–9 are recalculated to correspond to the heat-input rate of 10,000 Btu/(sq ft)(hr) specified for the preheater section. These calculations are repeated, as indicated in Table C and Fig. 178 for successive sections of 3, 3, 5, 5, and 10 tubes until the conditions at the inlet of tube 35 or the outlet of tube 36 are evaluated. It may be noted that at these conditions the rates of reaction are very low and that the number of moles of diphenyl is close to zero while a slight negative conversion to triphenyl is indicated. These differences from zero are less than the probable errors of the calculations and indicate that the assumption of six tubes for the reactor section is satisfactory.

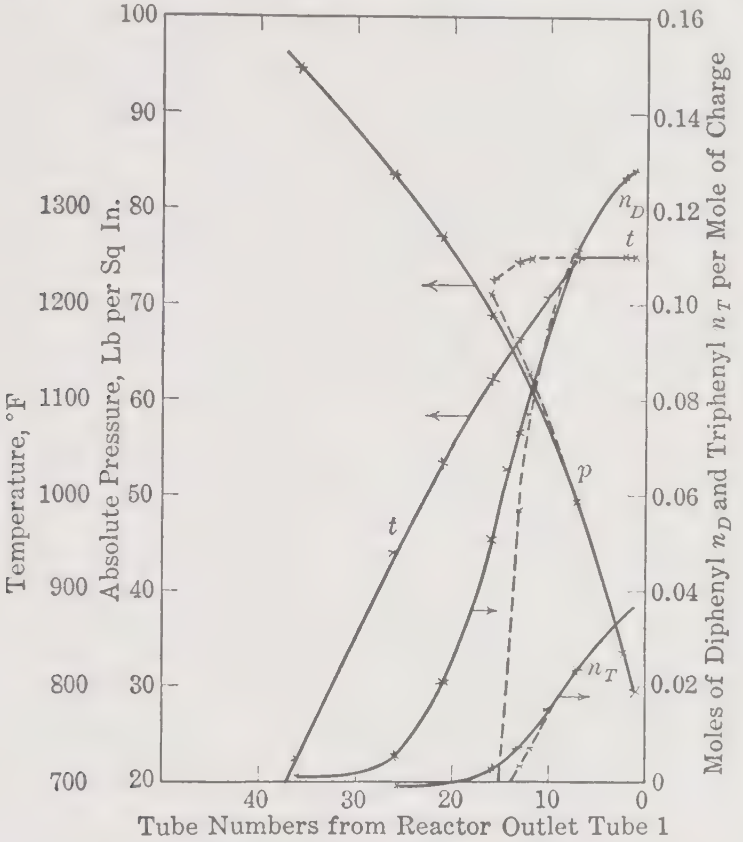

FIG. 178. Conditions at Tube Outlets of the Diphenyl Reactor and Preheater.

By extrapolating the temperature curve of Fig. 178 to 700°F the specified inlet temperature, it is seen that a total of 36 tubes is required. Thirty of these tubes are used in the preheater and six in the reactor sections. Extrapolation of the pressure curve indicates a pressure of 96 lb per sq in. at the inlet of tube 36 which is the inlet of the preheater.

The fortuitous choice of six tubes for the reactor section made further calculation unnecessary. If five or seven tubes had been assumed for this section, the corresponding calculated conversions at the preheater inlet would have been, respectively,

TABLE C

			←First Trial→						←Second Trial→			
1 Tube numbers, inclusive	1	2–6	7–11	12	13–15	7–9	10–12	13–15	16–20	21–25	26–35	36–
2 No. of tubes in section	1	5	5	1	3	3	3	3	5	5	10	..
3 $\Delta(1/S_v)10^4$	0.124	0.620	0.620	0.124	0.372	0.372	0.372	0.372	0.620	0.620	1.24	..
4 Heated area, sq ft	4.82	24.10	24.10	4.82	14.46	14.46	14.46	14.46	24.1	24.1	48.2	..
Outlet Conditions												
5 Temperature, °F	1250	1250	1250	1250	1245	1250	1207.7	1165.6	1120.7	1036.9	940.6	724.5
6 Abs. pressure, lb per sq in.	29.7	33.8	49.4	62.9	65.0	49.4	56.9	63.2	68.8	77.1	83.9	94.7
7 n_B, moles per mole feed	0.6336	0.6402	0.7051	0.8243	0.8761	0.7051	0.7663	0.8323	0.8911	0.9607	0.9917	0.9995
8 n_D	0.1280	0.1266	0.1117	0.0767	0.0571	0.1117	0.0943	0.0730	0.0510	0.0206	0.0058	0.0019
9 n_T	0.0368	0.0355	0.0238	0.0074	0.0032	0.0238	0.0150	0.0072	0.0023	0.0006	0.0011	0.0011
10 n_H	0.2016	0.1977	0.1594	0.0916	0.0636	0.1594	0.1244	0.0875	0.0556	0.0193	0.0036	0.0003
Estimated average conditions												
11 Temperature, °F	1250	1250	1250	1245	1230	1230	1185	1140	1080	990	830	..
12 Pressure, lb per sq in.	32	42	49	64	68	52	61	66.5	72	81	89	..
13 n_B	0.6400	0.6670	0.7460	0.8625	0.9270	0.7280	0.7880	0.8570	0.9255	0.9781	1.0000	..
14 n_D	0.1260	0.1200	0.1000	0.0640	0.0350	0.1060	0.0880	0.0640	0.0350	0.0120	0.0000	..
15 n_T	0.0360	0.0310	0.0180	0.0025	0.0010	0.0200	0.0120	0.0050	0.0015	0.0007	0.0000	..
16 n_H	0.1980	0.1820	0.1360	0.0710	0.0370	0.1460	0.1120	0.0740	0.0380	0.0106	0.0000	..
17 T_c' °R	914	922	944	975	992	939	956	975	992	1006	1011	..
18 p_c', lb per sq in.	581	591	618	656	678	612	632	655	677	694	701	..
19 μ_c', micropoises	267	272	285	303	313	282	292	303	313	321	324	..
20 T_r'	1.87	1.85	1.81	1.75	1.70	1.80	1.72	1.64	1.55	1.44	1.27	..
21 p_r'	0.055	0.071	0.079	0.096	0.10	0.085	0.096	0.101	0.106	0.106	0.127	..
22 μ_r'	0.78	0.78	0.77	0.77	0.76	0.77	0.76	0.73	0.70	0.64	0.57	..
23 μ', micropoises	208	212	220	233	263	217	222	222	219	206	185	..
24 z'	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	0.99	..
Ideal molal c_p												
25 Benzene	..	..	..	49.2	49.0	49.0	48.4	47.8	46.8	45.1	42.2	..
26 Diphenyl	..	..	..	94.0	93.7	93.7	92.4	91.0	89.1	86.0	..	..
27 Triphenyl	..	..	..	138.5	138	138	136	134	131	127	..	..
28 Hydrogen	..	..	..	7.2	7.2	7.2	7.2	7.2	7.2	7.1	..	..
29 Mean c_p^*	..	..	..	49.3	49.1	49.4	48.7	48.0	46.9	45.1	42.2	..
30 $c_p' - c_p^*$	..	..	..	0.1	0.1	0.1	0.1	0.1	0.2	0.2	0.6	..
31 c_p'	..	..	..	49.4	49.2	49.5	48.8	48.1	47.1	45.3	42.8	..
32 $(\Delta H_1)10^{-3}$, Btu per lb-mole	21.2	21.2	21.2	21.2	21.2	21.1	21.0	20.9	20.8	20.6	20.2	..
33 $(\Delta H_2)10^{-3}$, Btu per lb-mole	16.9	16.9	16.9	16.9	16.8	16.8	16.7	16.6	16.5	16.2	15.9	..
34 $k_1\nu\ddagger z'$, lb-mole (hr)(atm)² (359 cu ft)	300	300	300	280	245	245	160	100	53	17	1.7	..
35 $k_2\nu\ddagger z'$, lb-mole (hr)(atm)² (359 cu ft)	345	345	345	325	285	285	185	120	61	20	2.0	..
36 K_1	0.23	0.23	0.23	0.23	0.22	0.22	0.20	0.18	0.15	0.12	..	..
37 K_2	0.43	0.43	0.43	0.42	0.42	0.42	0.40	0.39	0.37	0.34	..	..
38 r_1 (lb-moles)/(hr)(359 cu ft)	427	857	1658	3843	4470	1408	1564	1449	1077	493	62.3	..
39 r_2	104	189	264	337	191	236	209	132	47	12	0	..
40 $-\Delta n_B$	0.0066	0.0649	0.1192	0.0518	0.1734	0.0612	0.0660	0.0588	0.0696	0.0310	0.0078	..
41 Δn_D	0.0014	0.0149	0.0350	0.0196	0.0760	0.0174	0.0213	0.0220	0.0304	0.0148	0.0039	..
42 Δn_T	0.0013	0.0117	0.0164	0.0042	0.0070	0.0088	0.0078	0.0049	0.0029	0.0005	0.0000	..
43 Δn_H	0.0039	0.0383	0.0678	0.0280	0.0902	0.0350	0.0369	0.0319	0.0363	0.0157	0.0039	..
44 $(\Delta H_1)(-\Delta n_B - \Delta n_T)/2$ Btu	56.3	565	1092	482	1830	555	611	562	693	312	77	..
45 $(\Delta H_2)(\Delta n_T)$ Btu	22	198	278	88	118	148	130	81	48	8	0	..
46 $q(10^3$ Btu)/hr	4.05	39.4	70.8	48.2	144.6	144.6	144.6	144.6	241	241	482	..
47 q/A Btu/(sq ft)(hr)	840	1630	2940	10,000	10,000	10,000	10,000	10,000	10,000	10,000	10,000	..
48 Δt °F	0	0	0	5.1	17.3	42.3	42.1	44.9	83.8	96.3	216.1	..
49 Δp lb per sq in.	4.1	15.61	13.5	2.1	5.9	7.5	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	..

greater or less than zero. In this case the final design could have been arrived at by repeating the calculations, starting from the preheater inlet with a pressure assumption based on the first calculations.

The problem of Illustration 13 is solved by a relatively complicated procedure which insures accurate results if reasonably small increments are considered. In many cases this degree of accuracy may be greater than justified, and many simplifications are possible, particularly for the preliminary designs necessary to explore various ranges of operating conditions. After experience is gained in such calculations, it is possible to estimate average conditions in succeeding sections with such accuracy that corrections are rarely required.

Optimum Reactor Design. The optimum reactor design for a given process is that which results in the manufacture of the desired product at the lowest cost. In arriving at the optimum design, costs and credits from all sources must be considered, including all fixed and operating charges, raw-material costs and by-product credits. A series of designs may be developed in which the basic design factors are systematically varied and the costs of the product from each design are calculated. The combination of design factors which produces the lowest over-all cost is then determined by graphical interpolation.

The principal design factors generally considered are composition, temperature, pressure, or concentration, and space velocity or time. Since the optimum value of any one of these factors is dependent on the values of the others, it is theoretically necessary to explore all possible combinations. This may be done by plotting production costs against space velocity at several different temperatures, all corresponding to a constant pressure. This procedure is then repeated for other pressures. The lowest product cost for each pressure is then plotted against pressure to determine the over-all optimum. The corresponding values of temperature and space velocity are determined by interpolation between the values at the optimum for each pressure.

Such a complete analysis is rarely carried out because of the great amount of work involved. A minimum of 27 design studies and corresponding product costs are required for exploration of the economic effects of all three variables. Instead of carrying out such detailed calculations it is common practice to establish approximate relationships between the optimum values of the different factors and to fix as many as possible by considerations of practical expediency. For example, in the reaction of Illustration 11, the temperature is fixed at the highest possible in the available materials. The space velocity corresponding to a given temperature and pressure is fixed by the specification of product purity which limits the conversion of benzene to approximately 37 per cent. With these factors fixed only the effects of different operating pressures need be investigated from an economic standpoint. A higher pressure is helpful in reducing the size of the reactor but introduces added costs of pumping and increases the cost per unit volume of the reactor. In order to determine the optimum pressure, designs are worked out for a series of pressures, and the costs are evaluated. In general, such economic optimum conditions are not critical, and operations can be carried on over a wide range of conditions with little change in costs. For this reason it is not necessary that the optimum be evaluated with a high order of accuracy. The general effects of the individual operating variables are as follows:

Temperature. In general the highest possible operating temperature is the most economical for endothermic reactions or for any operation in which reverse reactions are negligible. For exothermic reactions which approach equilibrium the problem is more complicated. In such case increasing the temperature increases the rate of reaction but at the same time makes the equilibrium composition less favorable. As a result a definite optimum temperature exists which for a specified space velocity and pressure will result in maximum conversion. Calculations of such optimum temperatures for catalytic systems are discussed on pages 1020 to 1028.

Pressure. Increased pressure increases the production rate or conversion of any reactor if reverse reactions are negligible. Where a decrease in number of moles accompanies the reaction, increased pressure also favors the equilibrium composition. However, where an increase in the number of moles is involved, an optimum pressure will result in maximum conversion if equilibrium is approached. This effect is similar to that of temperature.

Space Velocity. In a reactor operating at fixed temperature and pressure the extent of conversion is determined by the space velocity in a flow process or the time in a batch process. Reduction of space velocity increases conversion and reduces costs of recycling. On the other hand, the cost of the reactor is increased and frequently an increased formation of undesirable by-products results in a poorer ultimate yield of desired products.

Equivalent Reactor Volume. In experimental operations it is frequently difficult to maintain a constant temperature throughout a flow reactor or during the entire cycle of operation of a batch reactor. The rigorous interpretation of such data becomes complicated if large temperature differences are involved, particularly where reverse reactions are significant. For this reason it is important that isothermal conditions be approximated as closely as possible.

Where relatively small temperature differences exist in a flow reactor satisfactory results can be obtained by calculating the equivalent volume of the reactor which at a constant reference temperature T_b would produce the same conversion as the actual reactor with its varying temperatures. In order to calculate such an equivalent reactor volume V_b, it is necessary to assume an approximate value of the average enthalpy of activation $\Delta H_m^\ddagger$ of the reactions taking place. If an intermediate reference temperature is selected somewhat lower than the maximum temperature, the value of the calculated equivalent volume is not greatly affected by moderate errors in $\Delta H_m^\ddagger$. Where experimental data at two different temperature levels are available, the equivalent reactor volumes at the two reference temperatures are calculated from a trial or assumed value of $\Delta H_m^\ddagger$. Rate equations may then be developed by treating these data as though they were obtained in isothermal reactors operating at the reference temperatures, and a corrected value of $\Delta H_m^\ddagger$ is then calculated. If the assumed values were grossly in error the calculation is repeated.

The same principles may be followed in calculating the equivalent time of reaction in a batch process. From Equation (55) the time $d\tau_b$ required at reference temperature T_b to produce the conversion dx_A resulting from time $d\tau$ at the existing temperature T is given by the following equation

$$d\tau_b = d\tau(k/k_b) \tag{104}$$

where k and k_b are the reaction velocity constants at the existing and the reference temperatures, respectively. Similarly, from Equation (80) for a flow process,

$$d(V_r/F)_b = d(V_r/F)(k/k_b) \tag{105}$$

Combining (104) and (105) with (18) and neglecting deviations from ideal-gas behavior gives

$$d\tau_b = d\tau\left[e^{-\frac{\Delta H_m^\ddagger}{R}\left(\frac{1}{T}-\frac{1}{T_b}\right)}\right] \tag{106}$$

$$d(V_r/F)_b = d(V_r/F)\left[e^{-\frac{\Delta H_m^\ddagger}{R}\left(\frac{1}{T}-\frac{1}{T_b}\right)}\right] \tag{107}$$

Equations (106) and (107) may be integrated for a reactor or process of known temperature distribution. Thus,

$$\tau_b = \int_0^\tau e^{-\frac{\Delta H_m^\ddagger}{R}\left(\frac{1}{T}-\frac{1}{T_b}\right)}\,d\tau \tag{108}$$

$$(V_r/F)_b = \int_0^{V_r/F} e^{-\frac{\Delta H_m^\ddagger}{R}\left(\frac{1}{T}-\frac{1}{T_b}\right)}\,d(V_r/F) \tag{109}$$

In using Equations (108) and (109) it is convenient to plot a curve relating the factor $e^{-\frac{\Delta H_m^\ddagger}{R}\left(\frac{1}{T}-\frac{1}{T_b}\right)}$ on a logarithmic scale to temperature on a uniform scale for the particular reaction under consideration. The total equivalent time or volume in any reactor is then readily calculated from the known relationship between temperature and either τ or V_r by graphical integration of Equation (108) or (109). This is accomplished by plotting $e^{-\frac{\Delta H_m^\ddagger}{R}\left(\frac{1}{T}-\frac{1}{T_b}\right)}$ as ordinates against τ or V_r as abscissas and determining the area under the curve between the terminal values of τ or V_r. In this manner experimental data may be corrected to a base temperature to facilitate interpretation where temperatures were not constant. However, this procedure is subject to errors where several reactions occur simultaneously with different enthalpies of activation. For such systems a close approach to isothermal conditions is desirable.

Severity Factors. In dealing with reactor data and designs where both temperature and pressure vary it is frequently convenient to correlate conversions and yields in terms of a *severity factor* which is a measure of the severity of the over-all reaction conditions. This semiempirical approach is particularly desirable for complex reacting systems such as the cracking of petroleum where many reactions occur simultaneously and the complete compositions of both the charge and the products are generally unknown. Although there is much evidence that cracking occurs through complex chain reactions, the over-all result may be treated as approximately equivalent to a first-order reaction in which the reaction velocity constant diminishes as conversion of the charge progresses. Thus,

$$k = k_0(1 - ax) \tag{110}$$

where

k = effective average reaction velocity constant corresponding to the range of fractional conversions from 0 to x

k_0 = effective initial reaction velocity constant for the unconverted charge

a = a proportionality factor depending upon the characteristics of the charge

Equation (110) is frequently satisfactory only over moderate ranges of conversion. Where high conversions are involved the following alternate form,

$$k = k_0/(1 + a'x) \tag{111}$$

may give better correlations.

Combining Equations (110) and (84), taking n_{A0} as 1.0 and assuming $\nu_A = 1.0$ gives

$$\int_0^{V_r} k_0 \pi \frac{dV_r}{n_0 F} = \int_0^x \frac{(1 + \omega x)\, dx}{(1 - ax)(1 - x)} \tag{112}$$

If it is assumed that the fugacity coefficient of the activated complex $\nu^\ddagger$ is constant, k_0 may be expressed in terms of $(k_0)_b$, the initial reaction velocity constant at the reference conditions of temperature T_b and pressure π_B where the compressibility factor of the feed is z'_b. Thus, from Equation (18) written for the two temperatures,

$$k_0 = (k_0)_b \frac{z'_b}{z'} e^{-\frac{\Delta H^\ddagger_m}{R}\left(\frac{1}{T} - \frac{1}{T_b}\right)} \tag{113}$$

Combining (113) and (112) and evaluating the second integral, gives

$$(k_0)_b \int_0^{V_r} \frac{\pi z'_b}{z'} e^{-\frac{\Delta H^\ddagger_m}{R}\left(\frac{1}{T} - \frac{1}{T_b}\right)} \frac{dV_r}{n_0 F}$$

$$= \frac{a + \omega}{a(1 - a)} \ln (1 - ax) - \frac{(1 + \omega)}{(1 - a)} \ln (1 - x) = (k_0)_b F_s \tag{114}$$

The first integral of Equation (114) is a severity factor F_s referred to the base conditions T_b and unit pressure. This severity factor represents the reactor volume operating at unit pressure and the selected base temperature T_b which is equivalent to the actual reactor volume per unit molal feed rate. Its dimensions are (pressure)(vol)(time)/mole. It is evident that the severity factor is increased by increased pressure p and temperature T and is reduced by increase in the mean compressibility factor z' or the molal feed rate per unit volume of reactor, n_0F/V_r. If the reaction occurs under such conditions that variations in the compressibility factor may be neglected, the severity factor is readily determined from the distribution of temperature and pressure throughout the reactor. This procedure is indicated diagrammatically in Fig. 179 where reactor temperature and pressure are respectively plotted against V_r. From these two curves and the enthalpy of activation $\Delta H^\ddagger_m$ are derived a curve relating $\pi e^{-\frac{\Delta H^\ddagger_m}{R}\left(\frac{1}{T} - \frac{1}{T_b}\right)}$ to V_r/n_0F. The area under this curve is equal to the severity factor.

If the compressibility factor z' of the reacting mixture cannot be assumed to be constant, the severity factor must be evaluated by means of a stepwise integration similar to that demonstrated in Illustration 11. In this manner variations of the compressibility factor with temperature, pressure, and conversion are taken into account. These variations are particularly important if a portion of the reaction occurs with the charg-

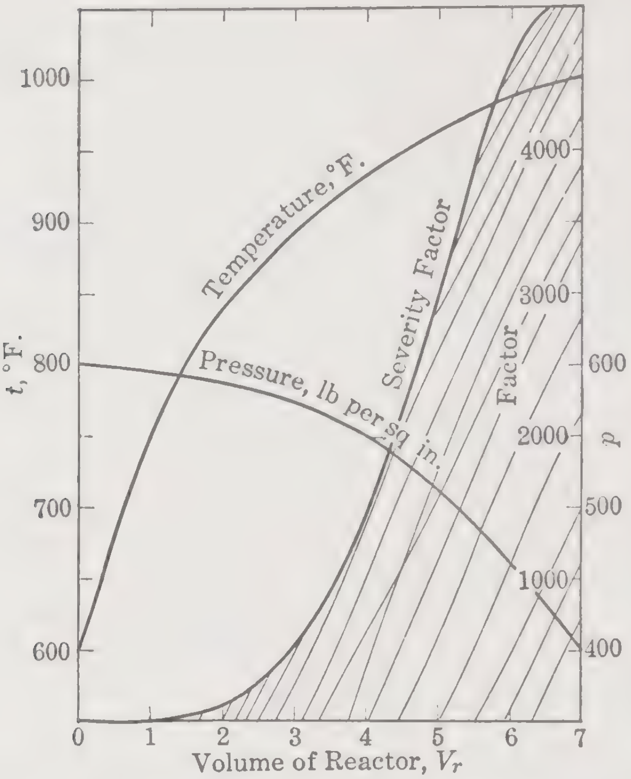

FIG. 179. Evaluation of Severity Factors where Compressibility Factor Changes are Negligible.

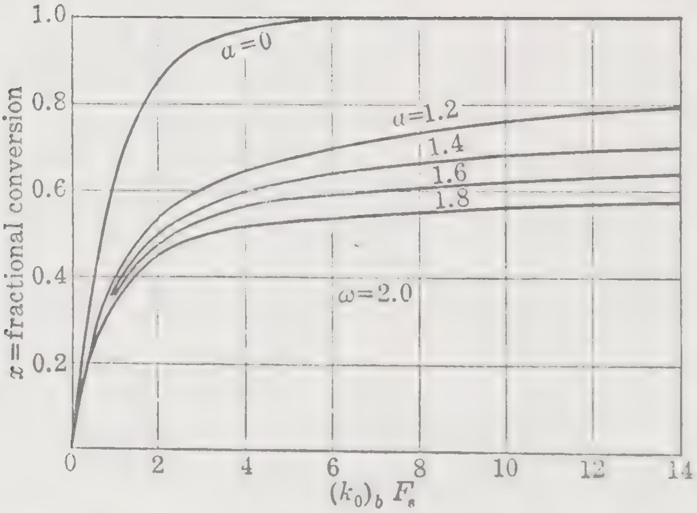

FIG. 180. Relation between Conversions and Severity Factors.

ing stock only partially vaporized. Under such conditions the compressibility factor z' is equal to pv/RT for the entire two-phase mixture and accordingly may vary widely with the degree of vaporization.

The severity factor may be employed as a basic factor for the correlation of conversions, yields, product distributions, and qualities in complex reacting systems. The relationship between the severity factor and conversion x may be obtained by evaluating the integral on the right side of Equation (112). In this manner a family of curves may be constructed such as is shown in Fig. 180. Each curve corresponds to a different class of feed stocks for which values of ω and a are specified. Where Equation (114) is not applicable, curves relating conversion to the severity factor may be empirically evaluated.

Similar severity factors may be defined and used for semiempirical correlations of rate and yield data in reaction systems which do not approximate first-order behavior. Such factors will generally involve a pressure term with an empirically determined exponent.

PREDICTION OF ENTROPY AND ENTHALPY OF ACTIVATION

Eyring and coworkers have developed detailed methods for predicting both the entropy and the enthalpy of activation. The enthalpy calculation is complicated and uncertain in its present state of development. The entropy of the activated complex is determined by the statistical methods outlined in Chapter XVII. This calculation requires that a completely defined structure be assigned to the activated complex with all atomic distances and vibration frequencies evaluated. General rules are not yet available for this procedure, and considerable latitude is exercised in the assignment of structures which result in calculated entropies and enthalpies in agreement with experimental values.

In view of the complexity and the judgment required in detailed calculations it appears that the best immediate engineering application of the theory of absolute reaction rates is in the rough approximation of entropy and enthalpy of activation. With an estimated entropy the enthalpy of activation may be calculated from a single determination of the reaction velocity constant where only one chemical step is involved. The resulting equation is useful for estimating the effect of temperature on the rate of reaction over limited temperature ranges, even though the entropy and energy of activation are considerably in error. For example, at 1000°K an error in entropy of activation of 10 units corresponds to an error in enthalpy of activation of 10 kcal per g-mole. The enthalpies of activation of high-temperature reactions range from 30 to 100 kcal per g-mole, and in several instances the disagreement between experimentally determined enthalpies of activation is greater than 10 kcal.

Similarly, if the enthalpy of activation is estimated from an empirical rule, the corresponding entropy of activation may be calculated from a single experimental result. If rules of the same degree of reliability are available for estimating both entropies and enthalpies of activation, the following procedure may be followed for arriving at a complete equation from a single experimental-reaction velocity constant:

1. Estimate the entropy of activation by the empirical rule.
2. Calculate the corresponding enthalpy of activation from the experimental-reaction velocity constant and Equation (17).
3. Estimate the enthalpy of activation by the empirical rule.
4. Average the enthalpies of steps 2 and 3.
5. Using the average enthalpy of activation calculate the corresponding entropy of activation from Equation (17).

Another useful application of approximate rules for estimating both entropy and enthalpy of activation is in the estimation of approximate relative reaction rates to serve as guides in selecting the rate-determining steps of chain reactions. Even though the absolute rates estimated in this manner are greatly in error, they may serve to eliminate the necessity of further consideration of reactions which are extremely fast or slow in comparison to the order of magnitude of the over-all rate. Methods for predicting reaction rates are reviewed by Daniels.[16]

Empirical Rules for Entropy of Activation. The following rules may be used for the rough estimation of the entropy of the activated complex at 298°K and 1 atm.

Reactions Unimolecular in Both Directions. Isomerization or rearrangement reactions of complex molecules which do not result in the formation or breaking of a ring appear generally to form an activated complex having a lower entropy than the reactant or product molecules. This is presumed to result from the formation of temporary multiple bonds in the complex which eliminate opportunities for internal rotation. The resulting loss in entropy is dependent on the moments of inertia and potential barriers of the groups whose rotation is stopped and also on the vibrational contributions added by the temporary bonds. For complex molecules containing more than ten atoms it may be assumed that an average loss in entropy of ten units accompanies the formation of the complex. The entropy of the activated complex is determined by averaging the results obtained on this basis from consideration of the forward and reverse reactions. Thus, for the reaction,

$$A \rightleftarrows X^{\ddagger} \rightleftarrows B$$

$$S^{\ddagger} = \frac{S_A + S_B}{2} - 10 \tag{115}$$

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[16] F. Daniels, *Ind. Eng. Chem.*, **35**, 504 (1943).

Then, for the forward reaction,

$$\Delta S^{\ddagger} = S^{\ddagger} - S_A \tag{116}$$

and the reverse reaction,

$$\Delta S^{\ddagger\prime} = S^{\ddagger\prime} - S_B \tag{117}$$

Unimolecular reactions resulting in ring closure would be expected to proceed at an abnormally slow rate because of the high decrease in entropy due to restrictions in internal rotations, whereas ring-opening reactions would be expected to proceed at an abnormally rapid rate for opposite reasons. For example, the decomposition of ethylene oxide results in ring breaking in the formation of the activated complex with an increase of 7.5 entropy units. Similarly, reactions which proceed by a chain mechanism proceed rapidly, in part owing to the increased entropy in the formation of free radicals.

Unimolecular–Bimolecular Reactions. Where a simple unimolecular reaction produces two product molecules, it appears that the entropy of the activated complex may be taken as equal to that of the reactant molecule. Thus, for the reaction,

$$A \rightleftarrows X^{\ddagger} \rightleftarrows R + S \tag{118}$$

For the forward reaction,

$$\Delta S^{\ddagger} = 0 \tag{119}$$

For the reverse reaction,

$$\Delta S^{\ddagger\prime} = S_A - S_R - S_S = -\Delta S \tag{120}$$

This rule is based on the finding of Daniels[16] who pointed out that the frequency factor $\mathbf{k}T/\mathbf{h}$ at 300°K is equal to $0.63(10^{13})$. From a survey of 28 of the most reliable unimolecular reactions Daniels[16] found that for 82 per cent the value of $\frac{\mathbf{k}T}{\mathbf{h}} e^{-\frac{\Delta S^{\ddagger}}{R}}$ ranged from 10^{12} to 10^{14} at 300°K, indicating that $\Delta S^{\ddagger}$ was very small.

Reactions Bimolecular in Both Directions. When two molecules form an activated complex which decomposes to form two other molecules without the formation or destruction of a ring, it may be assumed that for complex molecules the external rotational contribution to the entropy of the complex is equal to the sum of the rotational contributions of the reactants. On this basis the entropy changes accompanying the formation of the complex result from changes in the translational contributions and the vibrational and internal rotational contributions. The changes in the translational contributions are readily calculated from Equation (XVII–12), and it will be assumed that the formation of the complex is accompanied by an increase of four units in vibrational and internal rotational entropy. The entropy of the activated complex is taken as the average of the values obtained by applying these rules to the forward and reverse reactions. Thus, for the reaction, with each component in the ideal-gaseous state at 1 atm and 298°F

$$A + B \rightleftarrows X^{\ddagger} \rightleftarrows R + S$$

$$\begin{aligned} S_X^{\ddagger\prime} = {} & S_A + S_B + (\tfrac{3}{2}R \ln M_X + 26.00) - (\tfrac{3}{2}R \ln M_A + 26.00) \\ & - (\tfrac{3}{2}R \ln M_B + 26.00) + 4 = S_A + S_B \\ & + \tfrac{3}{2}R \ln \left(\frac{M_X}{M_A M_B}\right) - 22.0 \end{aligned} \tag{121}$$

Similarly,

$$S_{X_2}^{\ddagger} = S_R + S_S + \tfrac{3}{2}R \ln \frac{M_X}{M_R M_S} - 22.0 \tag{122}$$

where

$M_X, M_A, M_B \cdots$ = molecular weights of $X^{\ddagger}, A, B \cdots$

$$S_X^{\ddagger} = (S_{X1}^{\ddagger} + S_{X2}^{\ddagger})/2 \tag{123}$$

For the forward reaction,

$$\Delta S^{\ddagger} = S_X^{\ddagger} - S_A - S_B \tag{124}$$

For the reverse reaction,

$$\Delta S^{\ddagger\prime} = S_X^{\ddagger\prime} - S_R - S_S \tag{125}$$

Empirical Rules for Enthalpy of Activation. Empirical rules for estimating enthalpies of activation have been proposed by Hirschfelder[17] on the basis of the assumption that the energy of formation of a chemical bond in the ideal-gaseous state from the component elements as ideal monatomic gases is in general independent of the nature of compound in which it exists. On this basis values of bond energies have been developed which are given in Table LVI.[16] From this table approximate values of heats of reaction in the ideal-gaseous state may be obtained by subtracting the sum of all the energies of bond formation of the reactants from the corresponding sum of the products. However, the values obtained in this manner are less reliable for complex compounds than those obtained by the method of group contributions described in Chapter XVII for heats of formation.

Hirschfelder proposed the following rules relating to bond energies and enthalpies of activation. These rules must not be applied to the over-all result of a chain reaction but are applicable to any of the intermediate single steps.

[17] J. O. Hirschfelder, *J. Chem. Phys.*, **9**, 645 (1941).

Dissociation Reactions. In general, it may be assumed that the enthalpy of activation of the combination of two free radicals or atoms is zero under conditions which are thermodynamically unfavorable for their existence in appreciable concentrations. On this basis, for the dissociation of a molecule AB into atoms or radicals A and B according to the reaction,

$$AB \rightleftarrows A + B$$

$$\Delta H^{\ddagger} = \Delta H \tag{126}$$

$$\Delta H^{\ddagger\prime} = 0 \tag{127}$$

Reactions Bimolecular in Both Directions. Reactions of this type may be represented by the general equation:

$$AB + CD \rightleftarrows AC + BD$$

TABLE LVI

APPROXIMATE BOND ENERGIES[16]

Kcal per G-Mole Absorbed in Bond Rupture

C—H	92	C=C	122	=N—N=	33
C—Cl	79	C≡C	200	C—O	82
C—Br	58	H—H	102	C=O	188
C—I	44	O—H	113	Br—Br	45
C—C	77	N—H	96		

According to Hirschfelder the enthalpy of activation of such a reaction in the *exothermic direction* is equal to 28 per cent of the energy required to dissociate the reacting molecules. Thus,

$$\Delta H^{\ddagger} = 0.28(E_{AB} + E_{CD}) \quad \text{when} \quad \Delta H \text{ is negative} \tag{128}$$

$$\Delta H^{\ddagger\prime} = -\Delta H + \Delta H^{\ddagger} \tag{129}$$

Atomic–Molecular Reactions. Reactions between a free radical or an atom and a molecule may be represented by the general equation:

$$A + BC \rightleftarrows AB + C$$

Hirschfelder proposes that for *exothermic* reactions of this type

$$\Delta H^{\ddagger} = 0.05E_{BC} \quad \text{when} \quad \Delta H < 0 \tag{130}$$

$$\Delta H^{\ddagger\prime} = -\Delta H + \Delta H^{\ddagger} \tag{131}$$

These rules give results in fair agreement with the relatively few reliable experimental data which are available.

Illustration 14. Estimate the entropy of activation $\Delta S^{\ddagger}$ in concentration units of the formation of HI from gaseous hydrogen and iodine at a temperature of 298°K.

Solution: The entropies of the reactants and products at 298°K and 1 atm are obtained from Table XXXV, page 701.

$$S_{H_2} = 31.23 \qquad M_{H_2} = 2.0$$
$$S_{I_2} = 62.29 \qquad M_{I_2} = 254$$
$$S_{HI} = 49.36 \qquad M_{HI} = 128$$
$$H_2 + I_2 \rightleftharpoons (2HI)^{\ddagger} \rightleftharpoons 2HI$$

From Equation (122),

$$S^{\ddagger}_{X1} = 31.23 + 62.29 + 2.98 \ln \left(\frac{256}{(2)(254)} \right) - 22.0 = 69.5$$

$$S^{\ddagger}_{X2} = (2)(49.36) + 2.98 \ln \left(\frac{256}{(128)^2} \right) - 22.0 = 64.3$$

$$S^{\ddagger}_{X} = (69.5 + 64.3)/2 = 66.9$$

$$\Delta S^{\ddagger}_{(298°K)} = 66.9 - 31.23 - 62.29 = -26.6$$

Glasstone, Laidler, and Eyring[1] report a value of $\Delta S^{\ddagger}$ (300°K) = -20.3 for the reaction of Illustration 14. In this case the simple rule for estimating the entropy of activation led to an error of 6.3 units. For more complex molecules this error might be reduced somewhat by improved additivity of the rotational contribution, but it should be recognized that rules of this type may lead to errors of ten entropy units or more for simple reactions and are not applicable to the over-all results of chain reactions.

PROBLEMS

1. Calculate the reaction velocity constants from the following data of Schumacher[18] for the designated unimolecular reactions, assuming ideal behavior. Express rates in g-moles/(liter) (sec) with activities in atmospheres.

	T	$\Delta H^{\ddagger}$ *KCal per G-Mole*	$\Delta S^{\ddagger}$ *(Entropy Units)*
(*a*) Decomposition of dimethylether, CH_3OCH_3	780°K	56.95	2.5
(*b*) Decomposition of methyl azide, CH_3N_3	500°K	42.5	8.2
(*c*) Decomposition of tetramethyl silicane $Si(CH_3)_4$	950°K	76.9	2.2
(*d*) Decomposition of azo methane $CH_3N\ NCH_3$	600°K	48.8	10.8

Calculate the percentage error resulting from assuming that $\Delta S^{\ddagger} = 0$ in each of the afore-mentioned cases.

2. The kinetic and thermodynamic behavior of a reaction of the type $A + B = R + S$ in an ideal-gaseous system is expressed by the following data:

Reaction velocity constants:

$$k_{450°F} = 0.0061 \text{ g-mole/(liter)(atm}^2\text{)(sec)}$$
$$k_{500°F} = 0.0239 \text{ g-mole/(liter)(atm}^2\text{)(sec)}$$

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[18] H. J. Schumacher, "Chemische Gasreaktionen," T. Steinkopf (1938).

The standard enthalpy and entropy changes may be assumed to be constant over the temperature range of interest.

$$\Delta H^\circ = 8{,}400 \text{ cal per g-mole}$$
$$\Delta S^\circ = -2.31 \text{ cal per (g-mole)(°K)}$$

(*a*) Derive an equation for the reaction velocity constant of the forward reaction as a function of temperature.

(*b*) Evaluate $\Delta H^\ddagger$ and $\Delta S^\ddagger$.

(*c*) Evaluate an expression for the reaction velocity constant of the reverse reaction as a function of temperature.

3. The rate of a reaction is reported as $2.46(10^{-4})$ lb-mole/(hr) (cu ft). Express the rate in

(*a*) Molecules/(cu cm)(sec).

(*b*) G-moles/(liter)(sec).

4. In the rate equation,

$$r = k_c c_A^2$$
$$k_c = 0.0031 \text{ at } 700\text{°K}$$

where
$$r = \text{g-moles/(min)(22.41 liters)}$$
$$c = \text{g-moles/(22.41 liters)}$$

Calculate the value of k for the same reaction when $r = kp_A^2$.

$$r = \text{lb-moles/(cu ft)(min)}$$
$$p_A = \text{atmospheres}$$

5. A first-order reaction in an ideal-gaseous system at 680°R has a reaction velocity constant of 0.14 lb-mole/(359 cu ft)(atm)(hr). Calculate the corresponding value of k_c in 1/sec.

6. A third-order reaction in an ideal-gaseous system has a reaction velocity constant $k_c = 140$ (liters)^2/(g-mole)^2/(sec). Calculate the value of k in lb-moles/(359 cu ft)(atm)^3(hr) as a function of T°R.

7. The reaction velocity constant for the dimerization of butadiene is given by Vaughan[19] as $k_c = 9.2(10^9)e^{-\frac{23{,}900}{RT}}$ cc/(g-mole)(sec). Estimate the values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ at 600°K, assuming ideal behavior and a standard state of unit fugacity.

8. Glasstone, Laidler, and Eyring[1] report the reaction velocity constant for the isomerization of isostilbene as $6.0(10^{12})e^{-\frac{48{,}000}{RT}}$ reciprocal seconds. Calculate the values of $\Delta S^\ddagger$ and $\Delta H^\ddagger$ at 600°K for a standard state of 1 atm fugacity, assuming ideal behavior.

9. In the dimerization of ethylene, $\Delta c_p^\ddagger$ for the reaction is -6.0 cal per g-mole of complex. From Illustration 1 the value of $\Delta H^\ddagger$ is 32.73 kcal and that of $\Delta S^\ddagger$ is -35.00 both at 673°K and a standard state of 1 atm fugacity. Calculate the values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ at 1000°K and the corresponding value of the reaction velocity constant.

10. Hydrogen peroxide in aqueous solution is decomposed by the homogeneous catalytic action of alkalies with liberation of oxygen. The reaction is of the first order, and the reverse reaction is negligible. In a 0.04 normal NaOH solution at 60°C, k_c is 0.0389 per min; at 20°C, $k_c = 0.00106$.

A bleach bath of 2,000 kg contains H_2O_2 equivalent to an available oxygen content of 40 per cent by volume and NaOH equivalent to 0.04 normality. The density of the bath may be taken as 1.0.

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[19] W. E. Vaughan, *J. Am. Chem. Soc.*, **54**, 3863 (1932).

The percentage available oxygen content refers to the volume of oxygen gas at 1 atm, 0°C., which may be liberated from the hydrogen peroxide expressed as a percentage of the volume of the liquid. For a period of 1 hr at 60°C calculate:

(*a*) The percentage decomposition of hydrogen peroxide.

(*b*) The grams of H_2O_2 decomposed.

11. Five hundred grams of phosphine gas are heated in a tube at 672°C., 1 atm pressure, for 200 sec. Dissociation proceeds according to the reaction, $4PH_3(g) \rightarrow P_4(g) + 6H_2(g)$, and is of the first order. The reverse reaction is negligible. The reaction velocity constant k_c per sec is expressed as a function of temperature according to the following equation given by the International Critical Tables:

$$\log_{10} k_c = -\frac{18963}{T} + 2 \log_{10} T + 12.130 \quad \text{where } T \text{ is in degree Kelvin.}$$

Calculate:

(*a*) The grams of phosphorus formed.

(*b*) The time required to decompose 95 per cent of the phosphine at a temperature of 672°C.

12. The saponification of ethyl acetate by alkalies in aqueous solution is a relatively rapid reaction; the reverse reaction is negligible. For a second-order reaction the reaction velocity constant is given by the International Critical Tables where the initial normality of caustic soda is 0.05, as

$$\log_{10} k_c = -\frac{1780}{T} + 0.00754T + 5.83$$

where k_c is the reaction velocity constant in liter/(g-mole)(min) and T is in degrees Kelvin. Calculate the time required to saponify 98 per cent of the ester at 40°C when the initial concentration of ethyl acetate is 2.0 g per liter, and the initial normality of NaOH is 0.05.

13. The decomposition of nitrous oxide proceeds as a second-order reaction, $2N_2O \rightarrow 2N_2 + O_2$. The reverse reaction is negligible. At 895°C, the International Critical Tables give the value of k_c as 977 (cc)(g-mole)/sec. Calculate the time required to decompose 90 per cent of the N_2O at 895°C:

(*a*) When the volume is kept constant, initial pressure 1 atm.

(*b*) When the pressure is kept constant at 1 atm.

14. One hundred grams of acrolein are treated with 120 g of 1,3-butadiene in a 5-liter vessel to form 1, 2, 3, 6-tetrahydrobenzaldehyde. The weights of the aldehyde formed in various time intervals are given herewith for constant temperatures

Temperature	*Grams of Aldehyde Formed*	*Time, Min*	*Temperature*	*Grams of Aldehyde Formed*	*Time, Min*	*Temperature*	*Grams of Aldehyde Formed*	*Time, Min*
150°C	43	100	200°C	31	4	250°C	45	1
	73	200		44	8		63	2
	90	300		57	12		83	3
	109	400		68	16		96	4
	111	500		73	20		113	5
				83	24			

150, 200, and 250°C, respectively. Evaluate the reaction velocity constants for this reaction and the enthalpy of activation, $\Delta H^{\ddagger}$.

15. From the work of Cain and Nicoll[20] the following rate data were obtained on the decomposition of diazobenzene chloride in aqueous solution at 50°C:

$$C_6H_5N_2Cl \rightarrow C_6H_5Cl + N_2$$

The initial concentration of the diazo salt in solution is 10 g per liter, and the sample chosen liberates 58.3 cc of nitrogen at 50°C and atmospheric pressure when completely decomposed. Calculate the reaction velocity constant k_c for the first-order reaction:

Time (min)	6	9	12	14	18	20	22	24	26	30
Gas liberated (cubic centimeters)	19.3	26.0	32.6	36.0	41.3	43.3	45.0	46.5	48.4	50.35

From the following temperature data calculate the value of $\Delta H^{\ddagger}$:

t°C	20	30	40	50	60
k_c	0.00166	0.00678	0.0210	0.0688	0.251

The reverse reaction is negligible.

16. From the data of Table C, Illustration 9, page 848, evaluate the average reaction velocity constants of reactions (1) and (2) by graphical integration using equations similar to (94). Compare these results with those of Table D, page 850.

17. By reference to Illustration 10 calculate the values of the reaction velocity constants, k_{c4}, k'_{c4}, k_{c6} and k'_{c6} for the chain reaction involved in the hydrogenation of bromine gas from the following experimental data from Bodenstein and Lind.[21]

At 277.5°C, $a = 0.2881$; $b = 0.1517$.

a = initial concentration of hydrogen, gram-moles per 22.4 liters
b = initial concentration of bromine, gram-moles per 22.4 liters

τ	x	τ	x
120	0.0359	840	0.1227
240	0.0632	1020	0.1308
360	0.0811	1320	0.1389
480	0.0957	1680	0.1442

x = gram-moles of hydrogen or bromine reacted per 22.4 liters.

18. Dimethyl ether upon heating without catalysis decomposes by a substantially irreversible first-order reaction into CH_4, CO, and H_2. The reaction velocity constant is given in the International Critical Tables as $k_c = 1.55(10^{13})e^{-\frac{58,500}{RT}}$ (1/sec).

(*a*) One hundred grams of dimethyl ether are heated at 500°C at constant volume conditions in a closed retort of 120 liters capacity for a period of 30 min.

(1) Calculate the percentage conversion of the ether.

(2) Calculate the final pressure in the closed retort.

(*b*) One hundred grams of ether are heated in the same retort open to the atmosphere. The ether which escapes is not subject to further decomposition, and decomposition during preheating to 500°C may be neglected. The heating is continued for a period of 30 min at 500°C.

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[20] J. C. Cain and F. Nicoll, *Proc. Chem. Soc.*, **24**, 282 (1909).

[21] Bodenstein and Lind, *Z. Physik. Chem.*, **57**, 168 (1907).

(1) Develop a differential equation expressing the rate of disappearance of ether from the retort, both by reaction and expulsion, as a function of the number of gram-moles of ether n_e present at any time τ after the reaction temperature is reached.

(2) Calculate the percentage decomposition of the ether originally charged.

(3) Calculate the percentage of undecomposed ether lost by escape from the open retort.

(*c*) Dimethyl ether is passed at 500°C and 1 atm pressure in a continuous stream through a reacting cylinder of 120 liters capacity at a constant entering rate of 5 g per min. Calculate the percentage of decomposition of the ether.

19. From the data of Illustration 5 calculate the reactor volume required to produce 90 per cent decomposition of a stream of N_2O in a flow system operating at a temperature of 895°C and a pressure of 2.0 atm with a feed rate of 650 lb per hr.

20. From the data of Illustration 6 calculate the volume of the flow reactor required to produce 90 per cent of the equilibrium hydrolysis of the methyl acetate in the specified solution when fed at a rate of 150 gal per hr at a temperature of 25°C.

21. Ratchford and Fisher[22] found that methyl acetoxypropionate decomposes on heating to form methyl acrylate and acetic acid in accordance with the following equation:

$$CH_3COOCH(CH_3)COOCH_3 \rightarrow CH_3COOH + CH_2{:}CHCOOCH_3$$

The pyrolysis was found to approximate closely the behavior of a first-order unidirectional reaction having the following reaction velocity constant (T in degrees Kelvin):

$$k_c = 7.8(10^9)e^{-\frac{38,200}{RT}} \quad (1/\text{sec})$$

Calculate the volume of the flow reactor required to produce 65 per cent decomposition in a feed of methyl acetoxypropionate flowing at 650 lb per hr at a pressure of 4 atm and a temperature of 1100°F.

22. The viscosity of liquid benzene at 40°C and atmospheric pressure is given by the International Critical Tables as 0.492 centipoise. Estimate the viscosity of the liquid at 70°C. Estimate the viscosity of the vapor at 300°C and 3 atm pressure.

23. The viscosity of CO_2 gas is given by the International Critical Tables as 0.0157 centipoise at 40°C and 1 atm pressure. From Fig. 175 estimate the viscosity of CO_2 gas at 500°C and 5 atm pressure.

24. Estimate the viscosity of propyl butyrate vapors at a temperature of 250°C and a pressure of 1.0 atm from the following data:

Molecular weight	130
Critical temperature, °C	327
Liquid density, 15°C, g per cc	0.879

25. From the following data, estimate the viscosity of pyridine vapors at a temperature of 450°C and a pressure of 30 atm.:

Molecular weight	79
Critical temperature, °C	344
Critical pressure, atm	60

26. The International Critical Tables give the viscosity of H_2 as 0.0084 centipoise and of NH_3 gas as 0.0092 centipoise at 0°C and 1 atm pressure. Estimate the viscosity of a gas mixture containing 20 per cent H_2 and 80 per cent NH_3 at 12°C and

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[22] W. P. Ratchford and C. H. Fisher, *Ind. Eng. Chem.*, **37**, 382 (1945).

1 atm. Compare this result with the International Critical Tables value of 0.0104 centipoise for this mixture.

27. Vapors of sulfuryl chloride at 200°F and 1.2 atm are fed to a $1\frac{1}{2}$-inch reactor tube at a rate of 418 lb per hr. The reactor tube is heated at a rate of 5,000 Btu/(hr)(sq ft) based on the internal area. At elevated temperatures the SO_2Cl_2 decomposes by a first-order reaction to form $SO_2 + Cl_2$. It is desired to produce 98 per cent decomposition of the SO_2Cl_2 fed. The pressure drop in the reactor and the effect of the reverse reaction may be neglected. From the following data calculate the length of reactor tube required, and plot a curve relating temperature to tube length:

Dimensions of tube:

Nominal size	$1\frac{1}{2}$ in.
Inside diameter	1.334 in.
Outside diameter	1.50 in.
Inside cross-sectional area	1.398 sq in.
Surface per foot of length	
Inside	0.3491 sq ft
Outside	0.3925 sq ft

For the uncatalyzed reaction, values of k_c are reported by Smith.[23]

$$k_c = (6.427)10^{15} e^{-\frac{50,610}{RT}} \quad (1/\text{sec})$$

The heats of formation are reported by the *U.S. Bureau of Mines Bulletin* 406 (1937).

Components	SO_2Cl_2	SO_2	Cl_2
ΔH (formation) (gas) 298°K, cal/g-mole	−82,040	−70,920	0
Molecular weight	135	64	71

For the molal heat capacity of $Cl_2(g)$, Spencer and Justice[24] give

$$c_p = 7.5755 + (2.4244)(10^{-3})T - (0.965)(10^{-6})T^2; \quad T \text{ in } ^\circ\text{K}$$

No data are available for the heat capacity of sulfuryl chloride at high temperatures. The following approximate equation is estimated from low-temperature data by the methods of Chapter XVII and may be used in the range from 300 to 900°K:

$$c_p = 13.00 + (24.0)(10^{-3})T - (14.4)(10^{-6})T^2$$

28. Calculate the volume of the adiabatic reactor operating at a pressure of 1.2 atm with an outlet temperature of 750°F which would be required to produce a conversion of 49 per cent in the reaction of Problem 27, neglecting decomposition in the preheater and assuming:

(*a*) Uniformity of temperature as a result of mixing in the reactor.

(*b*) A progressive temperature change with negligible longitudinal mixing in the reactor.

Develop an equation expressing temperatures throughout the reactor as a function of conversion.

29. It is desired to design a tubular heater and reactor for the pyrolysis of propane to produce a mixture of ethylene and propylene. Substantially pure propane is to be charged through a preheater which delivers it at a temperature of 600°F and an absolute pressure not in excess of 60 lb per sq in. to the inlet of the reactor–heater. In order to avoid secondary and reverse reactions the absolute pressure at the outlet of the reactor is maintained at 20 lb per sq in. The gases from the reactor are compressed and fractionated to recover the desired products and substantially pure propane which is recycled to the heater and reactor. The design is to be based on a total propane feed to the reactor of 7000 lb per hr and a conversion per pass of 80 per cent, corresponding to a net fresh charge of 5600 lb per hr.

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[23] D. F. Smith, *J. Am. Chem. Soc.*, 47, 1862 (1925).

[24] H. M. Spencer and J. L. Justice, *J. Am. Chem. Soc.*, 56, 2311 (1934).

A trial design is to be prepared on the basis of passing the entire heater and reactor charge in a single stream through a series of uniformly sized tubes each 30 ft long and connected together with 180° return bends. Each return bend has a volume equal to $3.1d^3$ where d is the inside diameter of the tube. The equivalent length of a return bend is 60 diameters of straight pipe, and the heated length of each tube is 28.0 ft. Tubes are available with inside diameters varying by $\frac{1}{2}$-in. increments from 1 in. Since the maximum operating temperature permitted by the tube material is 1400°F, the heater will be designed to raise the charge to this temperature with a uniform heat input rate of 8000 Btu/(hr)(sq ft) based on the actually heated internal tube area. In order to obtain favorable heat-transfer conditions the tube diameter should be as small as possible without exceeding the allowable inlet pressure. In the reactor section a constant temperature of 1400°F will be maintained by varying the heat-input rate.

It is required to determine the diameter and numbers of tubes for the specified service and also the temperature, pressure, conversion, product distribution, and heat-input-rate distribution curves throughout the heater and reactor, using the data of Table LIV.

For determination of the proper tube size simplified preliminary analyses should be made in which secondary reactions are neglected and only the combined effects of the four primary reactions are considered. The tube size and inlet pressure arrived at in this manner are used as the basis of the detailed analysis which considers all reactions.

For both the preliminary and the detailed analyses it is convenient to plot working curves relating the density, viscosity, and specific heat of the reactant mixture to temperature and conversion. It is satisfactory for this purpose to plot one curve for pure propane and one for 80 per cent conversion, assuming the product distribution indicated in Fig. 172. Values for other conversions can be estimated by linear interpolation between these curves.

30. The total feed to the heater of a single-coil cracking unit similar in flow to Fig. 92, page 422, is a light gas oil having a gravity of 38° API and a characterization factor of 11.3.

This stock is charged to the inlet of the radiant section of the heater at a rate of 65,000 lb per hr, a temperature of 730°F, and a gauge pressure of 630 lb per sq in. The products leaving the heater enter the top of a vertical adiabatic-reaction chamber where a small amount of cold quench oil is introduced to prevent coke formation on the walls of the chamber.

The radiant section of the heater comprises 66 tubes each $3\frac{1}{4}$ in. internal diameter and 30 ft long connected with 180° return bends each having a volume of 0.06 cu ft. The volume of the reaction chamber is 600 cu ft, and its ratio of diameter to height is such that it may be assumed to operate with uniform conditions of temperature and pressure throughout.

The distribution of temperatures and pressures at the outlets of the indicated tubes are as follows. The tubes are numbered from the inlet of the radiant section of the heater.

Tube No.,	*Temperature,* °F	*Pressure, Lb per Sq In.*
Furnace Inlet	730	630
10	795	615
20	840	595
30	875	570
40	905	540
50	922	500
60	942	448
66	950	400
Reaction chamber	875	400

The cracking of this charging stock is found to produce 2.9 moles of products per mole of net charge converted. The reaction may be assumed to approximate a first-order reaction in accordance with Equation (111). At a temperature of 900°F the initial-reaction velocity constant in concentration units (k_c) is 0.0015 (1/sec), and the enthalpy of activation is 55,000 cal/(g-mole). The value of a' in Equation (111) is 1.6. Neglecting changes in the compressibility factor of the feed, calculate:

(*a*) The severity factors in (equivalent cu ft)(hr)/lb-mole of the heater and the reaction chamber using a base temperature of 900°F with pressures in atmospheres.

(*b*) The relationship between severity factor and conversion x.

(*c*) The conversion produced in the heater alone and in the heater plus the reaction chamber.

31. Estimate the value of $\Delta S^{\ddagger}$ in the formation of NOCl(g) from NO(g) and Cl_2(g) at 298.1°K. The absolute molal entropies at 298.1°K and 1 atm are as follows:

$$\text{NOCl(g)}, s^\circ = 63.00$$
$$\text{NO(g)}, s^\circ = 50.34$$
$$\text{Cl}_2\text{(g)}, s^\circ = 53.31$$

CHAPTER XIX

CATALYTIC REACTIONS

By definition, a catalyst is a substance which influences the rate of a reaction but is not one of the original reactants or final products. The catalyst must participate in intermediate steps in such a manner as to facilitate the over-all course of the reaction. In terms of the theory of absolute reaction rates the function of the catalyst is to reduce the positive free-energy change accompanying the formation of the activated complex. This may be brought about by the substitution of a sequence of steps, each having a low free energy of activation for a single step involving a high free energy of activation in the uncatalyzed reaction.

Although a catalyst may greatly alter the free-energy changes accompanying intermediate steps of a reaction, the over-all free-energy change is not so influenced but is dependent only upon the initial state of the reactants and the final state of the products. Thus, although the catalyst may change the rate of reaction it cannot influence the over-all free-energy change and, hence, the equilibrium conditions approached, except as it may influence the nature of the terminal reactants and products. Similarly, a catalyst is unable to cause any reaction to proceed under conditions not in agreement with the principles of thermodynamics. For example, by means of a catalyst it is possible to accelerate the low-temperature combustion of hydrogen with oxygen to form water. However, it is impossible for a catalyst to restore such a system to its original state by reversing the reaction at the same conditions.

It follows from thermodynamic principles and the theory of absolute-reaction rates that if a catalyst increases the rate of reaction in the forward direction a corresponding increase is produced in the rate of the reverse reaction. Thus, the net rate of change of the system in either direction is increased, but it is always in the direction of thermodynamic equilibrium.

It is believed that in general catalysts function through forming definite intermediate compounds with the reactants. The high degree of specificity of chemical combination is in agreement with the selectivity exhibited by catalysts in accelerating certain reactions in preference to others. This selective behavior is illustrated by the influence of different catalysts upon the decomposition of ethyl alcohol. In the presence of an alumina catalyst, ethylene and water vapor are formed, whereas, with a catalyst of metallic copper, acetaldehyde and hydrogen predominate. Thus,

$$C_2H_5OH \underset{Al_2O_3}{\overset{354°C}{\rightleftarrows}} C_2H_4 + H_2O \tag{1}$$

$$C_2H_5OH \underset{Cu}{\rightleftarrows} CH_3CHO + H_2 \tag{2}$$

The selectivity of a catalyst is also dependent upon temperature. For example, from the measurements of Alvarado[1] the decomposition of ethyl alcohol in the presence of activated alumina follows Equation (1) at 354°C, whereas at a lower temperature, 269°C, ether is the principal product according to the following reaction:

$$2C_2H_5OH \underset{Al_2O_3}{\overset{269°C}{\rightleftarrows}} (C_2H_5)_2O + H_2O \tag{3}$$

In many processes the selectivity of the catalyst is its most important property. By proper choice of catalyst it is possible to accelerate only the desired reactions and to minimize the formation of undesired by-products which would result if all reactions were equally increased in rate. The principles governing the selection and preparation of catalysts for specific purposes are not yet well understood, and many of the developments in this field are the result of elaborate exploration programs involving the trial of countless materials. This type of approach is being supplemented by more scientific methods as the understanding of catalysis increases and new data on the nature of catalysts are made available through developments such as true surface-area measurements, X-ray and electron diffraction patterns, and electron-microscope studies. The published theories and results of catalysis of all types have been summarized in considerable detail by Berkman, Morrell, and Egloff.[2]

The discussion herein presented is directed toward the development of methods for quantitatively correlating the behavior of a given catalyst as a function of the conditions under which it is used and for arriving at process designs which lead to optimum results for that particular catalyst. The principles of the selection and development of catalytic materials are treated only in a general manner, incidental to this principal objective.

Solid Catalysts. Solid catalysts which increase the rates of reactions whose reactants and products are either liquids or gases are extensively used in many important processes. It is believed that such solids function through the occurrence of intermediate reactions on their surfaces. As a result the extent and character of the surface are of primary importance in determining catalytic effectiveness. In general it is desirable that the catalyst shall have a large surface area per unit mass or volume and that this surface be relatively accessible to the fluid-reactant mixture through interconnected pores and openings. In addition to having a large accessible area, the surface itself must exhibit the desired selective activity.

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[1] Alvarado, *J. Am. Chem. Soc.*, **50**, 790 (1928).

[2] S. Berkman, J. C. Morrell, and G. Egloff, "Catalysis," Reinhold Publishing Corporation, New York (1940).

It was proposed by Taylor that reactions which are catalyzed by solids actually occur on the surfaces of the solids at points of high chemical activity which are termed *active centers*.[3] On this basis the activity of a catalytic surface is proportional to the number of active centers per unit area. There is evidence that in many cases this concentration of active centers is relatively low, as indicated by the extremely small quantities of " poisons " which are sufficient to destroy the activity of a catalyst.

The exact nature of an active center and the conditions which must be fulfilled in order that a point on the surface may become an active center remains the subject of much speculation. There is evidence that the interatomic spacing of the solid structure is important as well as its chemical constitution and lattice structure. Catalytic activity also has been found to increase with increased magnetic susceptibility in some cases. Other specific indexes to catalytic activity; such as various chemical tests and analyses; and physical characteristics; such as true density, diffraction patterns, magnetic properties, dielectric constant, and structure as revealed by the electron microscope; have been found useful. Methods developed by Emmett[3] and coworkers for the reliable measurement of surface areas are of great importance to these studies in distinguishing changes in activity due to alterations in area from changes attributable to the nature of the surface itself. At present, however, the only general index to specific catalytic activity is an actual performance test.

Since catalytic-reaction rates are dependent upon the extent of accessible surface, much attention is given to increasing both the area and accessibility of catalyst surfaces. One method of achieving this which currently is undergoing intensive development is the use of finely divided particles of catalysts suspended as a dust or slurry in the reacting stream. By use of high concentrations of suspended catalyst it is possible to obtain large effective areas on the basis of both volume of reactor and weight of catalyst. This method is particularly well adapted to processes requiring frequent regeneration of the catalyst. Another widely used method involves the formation of the catalyst into pellets having a porous spongy structure. In order to be most effective the pellets should have relatively large pores with thin walls continuously interconnected to provide free access of reactants to the interior surfaces.

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[3] National Research Council, " Twelfth Report of Committee on Catalysis," John Wiley & Sons (1940).

In so-called *unsupported* catalysts, the entire particle consists of the catalytic material which may be made by direct precipitation and drying of the catalyst to produce in its final form a highly porous solid gel structure. Silica gel is characteristic of this type. Another method of making unsupported catalysts is to grind the material to a fine powder and with the aid of binders to compress it into pellets. The noncatalytic material is then removed by a subsequent operation, such as heating, burning, or treatment with chemicals. Another method is to prepare pellets or crystals of a substance which is later transformed to a catalyst by chemical treatment. Metallic catalysts are produced in this manner by the low-temperature reduction of sulfides, oxides, and nitrates.

It is sometimes possible to obtain catalysts of high activity by producing a structure having an abnormal atomic spacing. This is accomplished by chemical treatment of a substance with a normal structure in order to remove certain atoms and leave a solid lattice with unusual atomic separations. For example, activated charcoal is prepared by charring peach pits, crystals of organic acids, and the like. A zinc–chromate catalyst is prepared by heating zinc–ammonium chromate, driving off ammonia and water, and leaving the zinc and chromium atoms as widely separated as in the original compound. In a similar manner copper–chromate catalyst is prepared from copper–ammonium chromate. Nickel catalysts are prepared by dissolving out the aluminum from a nickel–aluminum alloy leaving the nickel widely spaced. When such a catalyst is used industrially only a small amount of the aluminum may be removed at a time. A fresh catalytic surface is then subsequently formed by each further treatment with alkali. A remarkable lattice was produced by Langmuir and Blodgett[4] from barium stearate. Stearic acid was dissolved from a mixture leaving the barium stearate intact with its initial atomic displacement.

Supported catalysts, as their name implies, consist of a carrier substance having a suitable form and a large surface upon which the catalyst is deposited. Substances such as silica gel, activated alumina, pumice, charcoal, and kieselguhr are widely used for supports. The catalytic material may be deposited by impregnation with a solution, followed by treatment with other reagents to cause precipitation or modification by drying and reduction by heating or oxidation or other chemical treatment. The catalyst may be deposited either directly on a porous pellet of the support or on a powder which is subsequently compressed into a pellet, generally with a binder which is removed in a subsequent operation.

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[4] Langmuir, "Recent Advances in Surface Chemistry and Chemical Physics," Science Press (1939).

The activity of a catalyst surface is permanently destroyed by sintering or overheating which permit the atoms to lose their favorable separation and to attain normal spacing.

Mechanisms of Reactions Catalyzed by Solids. The general quantitative relationships involved in the catalysis of fluid reactions by solids are summarized in a recent paper by the authors[5] from which much of the following discussion is taken. As a basis for the development of rate equations, it is postulated that, when catalyzed by a solid, a liquid- or gas-phase chemical reaction actually occurs on the surface of the catalyst and involves the reaction of molecules or atoms which are chemically adsorbed on the active centers of the surface. From this viewpoint the catalyst increases the rate of reaction through its ability to adsorb the reactants in such a form that the activation energy necessary for reaction is reduced far below its value in the uncatalyzed reaction.

In order that a reactant in the main fluid phase may be converted catalytically to a product in the main fluid phase, it is necessary that the reactant be transferred from its position in the fluid to the catalytic interface, be activatedly adsorbed on the surface, and undergo reaction to form the adsorbed product. The product must then be desorbed and transferred from the interface to a position in the fluid phase. The rate at which each of these steps occurs influences the distribution of concentrations in the system and plays a part in determining the over-all rate. Because of the differences in the mechanisms involved, it is convenient to classify these steps as follows when dealing with catalysts in the form of porous particles:

1. The mass transfer of reactants and products to and from the gross exterior surface of the catalyst particle and the main body of the fluid.
2. The diffusional and flow transfer of reactants and products in and out of the pore structure of the catalyst particle when reaction takes place at interior interfaces.
3. The activated adsorption of reactants and the activated desorption of products at the catalytic interface.
4. The surface reaction of adsorbed reactants to form chemically adsorbed products.

It is evident that the rates of these four types of operations are dependent on widely different factors in addition to the concentrations or concentration gradients involved. Type 1 is determined by the flow characteristics of the system, such as the mass velocity of the fluid stream, the size of the particles, and the diffusional characteristics of the fluid. Type 2 is determined by the degree of porosity of the catalyst, the dimensions of the pores, the extent to which they are interconnected, the size of the particles, the diffusional characteristics of the system, and the rate at which the reaction occurs at the interface. Type 3 is determined by the character and extent of the catalytic surface, and by the specific activation energies required for the adsorption and desorption of each of the components of the fluid. Type 4 is determined by the nature and extent of the catalytic surface and by the activation energies required for the reaction on the surface.

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[5] O. A. Hougen and K. M. Watson, *Ind. Eng. Chem.*, **35**, 529 (1943).

The relative importance of these four operations in determining the over-all rate varies widely. Type 1 is important only when rapid reactions are dealt with or where flow conditions are unfavorable. Since the rate of this operation is little affected by temperature, its relative importance tends to vary for a particular system; it is frequently negligible at low and highly important at high temperatures. Type 2 is frequently negligible for catalysts of low activity in small particles with large interconnected pores and ceases to be a factor for nonporous catalysts having no internal surface. However, in the general case of an active catalyst in moderately large particles having large internal surfaces with restricted capillarity it may be of major importance.

Operations of types 3 and 4 are chemical phenomena generally involving relatively large enthalpies of activation and are therefore highly sensitive to temperature. The actual chemical transformations frequently proceed by several successive stages, each with its own characteristic rate. This is particularly true where several molecules are involved. Since chemical rates vary over wide ranges, it is improbable that the rates of any two steps of types 3 and 4 will be of equal order in any given system. For this reason in many cases it is permissible to consider only the slowest single step of types 3 and 4 and to assume that equilibrium is maintained in all other steps of these types. Under such conditions the slowest activated step may be termed the " rate-controlling step," and the over-all rate is determined by consideration of it in combination with the physical steps of types 1 and 2.

In order to calculate the rate at which a catalytic reaction proceeds it is necessary to develop quantitative expressions for the rates of each of the individual steps which contribute to the mechanism. This requires consideration of the fundamental principles of activated adsorption, surface reactions, mass and heat transfer, and diffusion in porous solids.

ACTIVATED ADSORPTION

In Chapter VII, page 149, it is pointed out that there are two types of adsorption, one referred to as van der Waals or physical adsorption and the other as *activated adsorption* or *chemisorption*. In the van der Waals type, adsorption results from physical-attractive forces similar to those causing the condensation of a vapor. Chemisorption, as the name implies, is believed to involve definite electron bonds corresponding to the formation of a chemical compound between the adsorbate and the surface. Like a chemical reaction, chemisorption is a highly specific phenomenon depending upon the chemical natures of the adsorbate and adsorbent.

The concept of chemisorption was introduced by Taylor in 1930. Since that time much attention has been devoted to it in the literature as summarized by Taylor,[3] and Glasstone, Laidler, and Eyring.[6] It is currently believed that activated adsorption occurs only on specific active centers which, as previously pointed out, may represent only a small fraction of the total surface. On this basis the maximum capacity of a surface for a specific chemisorption is frequently much less than the amount of adsorbate required to form a monomolecular layer. By van der Waals adsorption it is possible to adsorb much larger quantities which form layers several molecules in thickness or result in capillary condensation.

Because of the larger energy changes involved in the formation of valence bonds the enthalpy changes accompanying chemisorption are generally highly negative, in the range of -10 to -100 kcal per g-mole. The enthalpy change of van der Waals adsorption is of the same order as the heat of condensation, in the range of -5 to -10 kcal per g-mole. It follows that the effect of temperature in diminishing the quantity of adsorbate at equilibrium is greater for activated than for van der Waals adsorption.

The most significant difference between van der Waals and activated adsorption is in the rate at which equilibrium is approached. Activated adsorption, as the name implies, requires a definite energy of activation which corresponds to relatively slow rates of adsorption. These rates are greatly affected by changes in temperature, just as is the case of any chemical reaction.

Although van der Waals adsorption may be considered as requiring an activation energy[3] its value is so low that in general it may be assumed that equilibrium is reached instantly at the interface and that observed rates of physical adsorption are largely determined by the accompanying diffusional phenomena.

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[6] "Theory of Rate Processes," Glasstone, Laidler, and Eyring, McGraw-Hill Book Company, New York (1941).

Both activated and van der Waals adsorption may be encountered in a single system, although they are frequently important in different ranges of temperature. In general, van der Waals adsorption becomes very small at temperatures not greatly above the critical temperature of the adsorbate. Much higher temperatures may be required in order that activated adsorption may proceed at a significant rate. This effect is shown diagrammatically in Fig. 181 in which quantity adsorbed at equilibrium under a constant pressure is plotted against temperature. For the system represented, the quantity which is chemisorbed at equilibrium approaches a maximum, corresponding to reaction with all available centers, at a relatively high temperature where the amount of van der Waals adsorption is negligible. At lower temperatures van der Waals adsorption becomes increasingly important.

Because of the low rates of activated adsorption at low temperatures, apparent total-adsorption curves of the form indicated by the broken line of Fig. 181 are frequently observed. Such regions of minimum adsorption are believed to result from failure to attain equilibrium chemisorption. The position of the broken-line curve of Fig. 181 is therefore dependent upon the time allowed for adsorption.

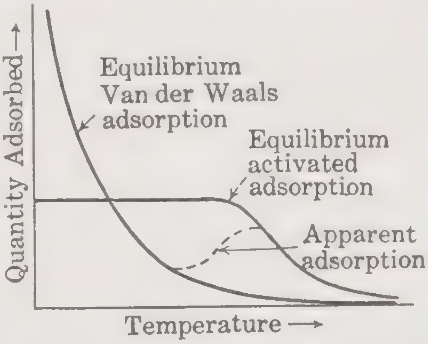

FIG. 181. Van der Waals and Activated Adsorption.

It is evident that measurements of either adsorption-equilibrium quantities or rates of total adsorption may represent a complicated combination of activated and van der Waals effects, unless there happens to be a wide temperature range in which van der Waals adsorption is negligible in quantity and chemisorption is negligible in rate. In the general case where such a separation does not exist, the interpretation of activated-adsorption data is difficult. This problem is further complicated by the observation that more than one type of activated adsorption of a single component may occur simultaneously on a given surface, presumably because of the existence of different types of active centers. The different types of adsorption may be effective in different temperature ranges. In such cases it is possible to obtain apparent adsorption-equilibrium curves which show two or more minima similar to that of Fig. 181.

In summary, van der Waals adsorption is characterized by high rates at low temperatures, large quantities of adsorbate, low heats of adsorption, and a relatively low degree of specificity. Activated adsorption on the other hand is characterized by low rates and high energies of activation, low quantities of adsorbate, high heats of adsorption, and a high degree of specificity.

Chemisorption Rates and Equilibria. In the development of rate equations for simple activated adsorption, it may be assumed that a unit area of surface offers L' active centers on which adsorption may occur and that all of these centers behave similarly. The rate of adsorption per unit area of a component A from a fluid in contact with the surface is then proportional to its activity a_{Ai} in the fluid at the interface and to the concentration c_l' of vacant active centers per unit area of surface. Since the actual surface area of porous materials is generally unknown, it is convenient to express reaction rates in moles formed per unit time per unit mass of solid having a surface area a_m. It is also convenient to express the number of active centers per unit mass in molal rather than molecular units. Thus L, the number of molal active centers per unit mass is equal to $L'a_m/N$ where N is the Avogadro number. Similarly the concentration of vacant active centers may be expressed in molal units per unit mass and designated as c_l. On this basis,

$$r_A = k_A a_{Ai} c_l \tag{4}$$

where r_A = rate of adsorption of A, moles per unit time per unit mass
k_A = adsorption velocity constant of A
a_{Ai} = activity of A in the fluid at the interface, in concentration units
c_l = molal concentration of vacant active centers per unit mass

Since chemisorption is a reversible phenomenon, component A is also desorbed from the surface at a rate proportional to the concentration of adsorbed molecules on the surface. Thus,

$$r_A' = k_A' c_A \tag{5}$$

where c_A = molal concentration of adsorbed A, moles per unit mass. The net rate of adsorption is then the difference between the rate of adsorption and desorption, or

$$r = k_A a_{Ai} c_l - k_A' c_A \tag{6}$$

When adsorption equilibrium is reached the net rate of adsorption becomes zero, and

$$\frac{c_A}{a_{Ai} c_l} = \frac{k_A}{k_A'} = K_A \tag{7}$$

where K_A = adsorption-equilibrium constant of A.

If (6) and (7) are combined, an expression is obtained for the net rate of adsorption where all sites are equally accessible.

$$r = k_A\left(a_{Ai}c_l - \frac{c_A}{K_A}\right) = k_A c_l(a_{Ai} - a^*_{Ai}) \tag{7a}$$

where a^*_{Ai} = activity of component A in equilibrium with the activatedly adsorbed molecules

The fraction of available sites c_l/L can be expressed in terms of the number of moles adsorbed per unit mass, thus:

$$\frac{c_l}{L} = 1 - \frac{n_A}{n^*_A} = \theta_l \tag{7b}$$

where n_A = moles of A adsorbed per unit mass of catalyst
n^*_A = moles of A adsorbed per unit mass of catalyst when all sites are covered
θ_l = fraction of available sites not covered

Where all the active sites are not equally accessible as when the adsorbent is in pellet form, an effectiveness factor E_A should be included, as discussed later.

If component A is in admixture with other components B, R, S, and I which are also adsorbed on active centers of the same type, rate and equilibrium equations similar to (6) and (7) may be written for each component. Then,

$$c_l = L - (c_A + c_B + c_I + \cdots) \tag{8}$$

At equilibrium conditions each of the adsorbate concentration terms in Equation (8) may be replaced by an expression similar to that obtained by solving Equation (7) for c_A:

$$c_l = L - c_l(a_{Ai}K_A + a_{Bi}K_B + a_{Ii}K_I + \cdots) \tag{9}$$

$$c_l = \frac{L}{(1 + a_{Ai}K_A + a_{Bi}K_B + a_{Ii}K_I + \cdots)} \tag{10}$$

An expression for the equilibrium surface concentration of A in terms of interfacial fluid activities is obtained by combining Equations (7) and (10):

$$c_A = \frac{a_{Ai}K_AL}{(1 + a_{Ai}K_A + a_{Bi}K_B + a_{Ii}K_I + \cdots)} \tag{11}$$

Similar equations may be written for the equilibrium surface concentrations of the other components of the mixture.

The theory of absolute-reaction rates is applicable to chemisorption in the same manner as to homogeneous reactions. It is assumed that chemisorption takes place through the formation of an activated complex with the active center. Thus, if l represents an active center the adsorption of A is represented by

$$A + l \rightleftarrows Al^{\ddagger} \rightarrow Al$$

If it is assumed that the activities of the adsorbed constituents are equal to their molal concentrations per unit mass of adsorbent, the reaction velocity constant of this reaction per unit mass of adsorbent is,

$$k_A = \frac{\mathbf{k}T}{\mathbf{h}} e^{-\frac{\Delta H_A^{\ddagger}}{RT} + \frac{\Delta S_A^{\ddagger}}{R}} \tag{12}$$

where $\Delta H_A^{\ddagger}$ and $\Delta S_A^{\ddagger}$ = the enthalpy and entropy of activation of the adsorption reaction.

Similarly, for desorption,

$$k'_A = \frac{\mathbf{k}T}{\mathbf{h}} e^{-\frac{\Delta H_A^{\ddagger\prime}}{RT} + \frac{\Delta S_A^{\ddagger\prime}}{R}} \tag{13}$$

Combining (7), (12), and (13) gives

$$K_A = e^{\frac{-(\Delta H_A^{\ddagger} - \Delta H_A^{\ddagger\prime})}{RT} + \frac{\Delta S_A^{\ddagger} - \Delta S_A^{\ddagger\prime}}{R}} = e^{\frac{-\Delta H_A^{\circ}}{RT} + \frac{\Delta S_A^{\circ}}{R}} \tag{14}$$

where $\Delta H_A^{\circ} = \Delta H_A^{\ddagger} - \Delta H_A^{\ddagger\prime}$ = the standard enthalpy change of adsorption

$\Delta S_A^{\circ} = \Delta S_A^{\ddagger} - \Delta S_A^{\ddagger\prime}$ = the standard entropy change of adsorption

Chemisorption with Dissociation. There is evidence that certain species of molecules are dissociated during chemisorption. For example, hydrogen and nitrogen molecules are dissociated to atoms when adsorbed on the surfaces of some materials.

Although other mechanisms are possible, Glasstone, Laidler, and Eyring[6] suggest that, where a molecule is dissociated during adsorption, it is commonly first adsorbed on a dual adsorption site consisting of two adjacent active centers. This adsorbed molecule then decomposes, and the atoms jump to two vacant active centers. Thus, if A_2 is a molecule which dissociates into two A atoms and l_2 is a dual adsorption site,

$$A_2 + l_2 \rightleftarrows A_2l_2$$
$$A_2l_2 + 2l \rightleftarrows 2Al + l_2$$

It is believed that the first step is rate-controlling and that equilibrium is maintained in the second. Then if r is expressed in moles of A_2,

$$r = k_{A_2} a_{A_2 i} c_{l_2} - k'_{A_2} c_{A_2 l_2} \tag{15}$$

Since the second step maintains equilibrium,

$$c_{A_2 l_2} = \frac{c_{Al}^2 c_{l_2}}{K'_A c_l^2} \tag{16}$$

where K'_A = equilibrium constant of the dissociation step.

In order to develop an expression for c_{l_2}, the molal concentration of dual adsorption sites, it is assumed that the active centers are arranged on the surface in a regular geometric pattern such that each site is surrounded by s equidistant adjacent sites. Thus, if the active centers are situated at the corners of squares, $s = 4$, whereas, if they are at the corners of equilateral triangles, $s = 6$.

If θ_l is the fraction of active centers unoccupied, an average center has adjacent to it $\theta_l s$ vacant centers. The total concentration of pairs of adjacent vacant active centers which are dual adsorption sites is then one-half the product of the concentration of vacant centers and the average number of adjacent vacant sites. The factor of one half results from the fact that, in the summation represented by the product of the concentration and fraction of vacancy terms, each pair of vacant active centers is counted twice.

$$c'_{l_2} = \frac{s\theta_l c'_l}{2} = \frac{s(c'_l)^2}{2L'} \tag{17}$$

where c'_{l_2} = concentration of dual sites per unit area
θ_l = fraction of active centers unoccupied
s = number of equidistant active centers adjacent to each center

Equation (17) also may be written in terms of molal concentrations per unit mass.

$$c_{l_2} = \frac{sc_l^2}{2L} \tag{18}$$

Combining (15), (16), and (18) yields

$$r = \frac{s}{2L}\left(k_{A_2} a_{A_2 i} c_l^2 - k'_{A_2}\frac{c_{Al}^2}{K'_A}\right) \tag{19}$$

At equilibrium,

$$\frac{c_{Al}^2}{a_{A_2 i} c_l^2} = \frac{k_{A_2} K'_A}{k'_{A_2}} = K_{A_2} \tag{20}$$

$$c_A = c_{Al} = c_l \sqrt{a_{A_2 i} K_{A_2}} \tag{21}$$

If A is adsorbed with dissociation from a mixture also containing components B and I, an expression similar to Equation (11) may be developed for adsorption-equilibrium conditions:

$$c_A = \frac{\sqrt{a_{A_2i}K_{A_2}}L}{1 + \sqrt{a_{A_2i}K_{A_2}} + a_{Bi}K_B + a_{Ii}K_I + \cdots} \tag{22}$$

It is evident by comparing Equations (11) and (22) that, if a molecule dissociates as it is adsorbed, the square root of the product of its activity times its adsorption-equilibrium constant appears in all adsorption-equilibrium expressions in place of the first power of this product.

The net rate of adsorption on dual active sites in the absence of dissociation and where all sites are equally accessible may be written from Equation (19) as

$$r = \frac{s}{2L} k_{A_2}c_l^2(a_{A_2i} - a_{A_2i}^*) \tag{22a}$$

where $a_{A_2i}^*$ is the activity of component A_2 at the interface in equilibrium with the adsorbed molecules.

The fraction of available single sites θ_l can be expressed in terms of the number of moles adsorbed per unit mass, thus:

$$\frac{c_l}{L} = 1 - \frac{n_{A_2}}{n_{A_2}^*} = \theta_l \tag{22b}$$

where n_{A_2} = mole of A_2 adsorbed per unit mass of catalyst
$n_{A_2}^*$ = moles of A_2 adsorbed per unit mass of catalyst when all sites are covered

From Equations (22a) and (22b),

$$r = \frac{s}{2} k_{A_2}L\theta_l^2(a_{A_2i} - a_{A_2i}^*) \tag{22c}$$

Limitations of Simple Adsorption Theory. In the derivation of Equations (4) to (22) it was assumed that all active centers have the same activity and undergo the same reaction in chemisorption. It is also assumed that the enthalpy and entropy changes accompanying chemisorption are constant, independent of the amount adsorbed. Experimental data on adsorption rates and equilibria indicate considerable deviation from both of these assumptions. The heat of adsorption is frequently found to become less negative as the amount adsorbed increases. There is also evidence of varying activity of the centers.

The observed variations in heat of adsorption are attributed both to variation in the character of the active centers and to interaction between the adsorbed molecules. Numerous modifications[6,7] of the fundamental adsorption equations which have been proposed take these effects into account and give improved agreement with experimental data. However, no simple form has been developed which has proved applicable to all systems. This difficulty probably results from the fact previously mentioned that observed adsorption data generally represent a complex combination of several simultaneous phenomena. Thus a single adsorbate may undergo simultaneously two or more types of activated adsorption together with some van der Waals adsorption. For this reason adsorption data for a particular system frequently are in better agreement with various empirical equations of logarithmic or exponential form than with the simple equations given.

The failure of Equations (5) to (22) to represent accurately data on the adsorption of pure components does not of necessity invalidate their application to the adsorption step of chemical reactions. It is probable that such an adsorption step in a particular reaction involves only active centers of a restricted degree of activity. The fundamental equations may accurately represent this single type of chemisorption while failing to apply to the composite effects of it and other types. The rate and equilibrium constants of such a single effective or apparent adsorption step must be evaluated from reaction-rate data by methods described in following sections. Such constants are effective average values for the range of conditions on which their evaluation is based and may show some lack of constancy over wide ranges. However, useful rate equations can be developed in this manner, with the assumption of simple adsorption relationships.

Furthermore, the distinction should be made between reaction rates proceeding at a steady state as do most reactions in flow systems and reaction rates of adsorption where no other reactions are involved. In the latter case, a nonsteady state is realized as the gas is gradually adsorbed with a rate diminishing to zero, whereas in the former case the reaction rates are constant requiring also that the amount adsorbed is not undergoing change.

SURFACE REACTIONS

When a reaction is catalyzed by a solid it is presumed that the actual combination of the reactants occurs on the surface of the solid. Such surface reactions may take place either between an adsorbed reactant molecule and a molecule in the fluid phase or between adsorbed molecules on adjacently situated active centers. With the latter mechanism

[7] S. Brunauer, K. S. Love, and R. G. Keenan, *J. Am. Chem. Soc.*, 64, 751 (1942).

a reaction proceeds at rates proportional to the concentrations of adjacently adsorbed reactants. Thus, if adsorbed molecule A reacts with adsorbed molecule B, the rate of the reaction is proportional to the number of pairs of adjacently adsorbed A and B molecules per unit area of surface. Similarly, if in a monomolecular reaction, adsorbed molecule A reacts with a vacant active center to form a complex which subsequently breaks down to form two adsorbed product molecules, the rate of the reaction is proportional to the number per unit area of A molecules adsorbed adjacent to vacant active centers.

If the arrangement of active centers is such that each is surrounded by s equidistant centers, an average adsorbed molecule of A has adjacent to it $s\theta_l$ vacant centers, where θ_l is the fraction of the total centers which is vacant. Similarly, $s\theta_B$ molecules of B are adjacent to each adsorbed A molecule, where θ_B is the fraction of the total centers which is occupied by adsorbed B molecules. Then by the type of summation obtained in deriving Equation (22), the surface concentration of A molecules and vacant active centers adjacent to each other becomes $sc'_A\theta_l$, and the concentration of A and B molecules adsorbed in adjacent positions becomes $sc'_A\theta_B$. Since θ_l equals c'_l/L' and θ_B equals c'_B/L',

$$c'_{Al} = \frac{s}{L'}\,c'_A c'_l \tag{23}$$

$$c'_{AB} = \frac{s}{L'}\,c'_A c'_B \tag{24}$$

where c'_{Al} = surface concentration of pairs of adsorbed A molecules and vacant centers in adjacent positions

c'_{AB} = surface concentration of pairs of adsorbed A and B molecules in adjacent positions

Equations (23) and (24) may be similarly written with concentrations c_{Al} and c_{AB} in moles per unit mass.

The rate of a monomolecular surface reaction involving interaction of an adsorbed A molecule and a vacant active center then becomes

$$r = kc_{Al} = k\frac{s}{L}\,c_A c_l \tag{25}$$

Similarly, for a surface reaction between adsorbed A and B molecules:

$$r = kc_{AB} = \frac{ks}{L}\,c_A c_B \tag{26}$$

If products R and S are formed, the net rate of the forward reaction on the surface is expressed by

$$r = \frac{ks}{L}\left(c_A c_B - \frac{c_R c_S}{K'}\right) \tag{27}$$

where K' = the equilibrium constant of the surface reaction = $c_R c_S / c_A c_B$ at equilibrium

If the surface reaction results from direct combination of an adsorbed molecule A with a molecule of B from the fluid phase, the rate is proportional to the concentration of adsorbed A molecules and to the activity of B in the fluid phase at the interface. Thus, in this case,

$$r = k a_{Bi} c_A \tag{28}$$

General Surface Rate Equations. On the basis of the principles discussed in the preceding sections, a general equation may be developed for the following surface reaction:

$$A + B \rightleftarrows R$$

In the general case the system will include inert components in the fluid phase represented by I. . . .

The net rate of the forward reaction is the difference between the rates of the forward and reverse reactions which are represented by Equations (26) and (25), respectively. Thus,

$$r = \frac{s}{L}\,(k c_A c_B - k' c_R c_l) \tag{29}$$

The surface concentrations may be expressed in terms of the activities in the fluid at the interface from Equations (4) and (5). Thus, the net rate of adsorption of component A is equal to the over-all rate of reaction. This net adsorption rate is the difference between the rates of adsorption and desorption, or

$$\begin{aligned} r &= k_A a_{Ai} c_l - k'_A c_A = k'_A(K_A a_{Ai} c_l - c_A) \\ c_A &= K_A a_{Ai} c_l - r/k'_A \end{aligned} \tag{30}$$

Similar expressions may be written for the other reactant and product adsorptions, and substituted in Equation (29):

$$r = \frac{s}{L}\left[k\left(K_A a_{Ai} c_l - \frac{r}{k'_A}\right)\left(K_B a_{Bi} c_l - \frac{r}{k'_B}\right) - k'\left(K_R a_{Ri} c_l + \frac{r}{k'_R}\right) c_l\right] \tag{31}$$

The concentration of vacant centers also may be expressed in terms of fluid-phase activities at the interface:

$$\begin{aligned} c_l &= L - (c_A + c_B + c_R + c_I + \cdots) \\ &= L - c_l(K_A a_{Ai} + K_B a_{Bi} + K_R a_{Ri} + K_I a_{Ii} + \cdots) \\ &\qquad + r\left(\frac{1}{k'_A} + \frac{1}{k'_B} - \frac{1}{k'_R}\right) \\ &= \frac{L + r\left(\dfrac{1}{k'_A} + \dfrac{1}{k'_B} - \dfrac{1}{k'_R}\right)}{(1 + K_A a_{Ai} + K_B a_{Bi} + K_R a_{Ri} + K_I a_{Ii} + \cdots)} \end{aligned} \tag{32}$$

Combining Equations (31) and (32) yields a complete expression for the rate of reaction in terms only of activities in the fluid at the interface and the constants of the system. If the constants were all evaluated, the equation could be solved graphically for the rate at specified conditions. However, in general this complete equation involving the rates of all adsorption steps as well as the rate of the surface reaction is so cumbersome as to be of little value.

As previously mentioned, in many cases it is satisfactory to assume that the rate is controlled by a single slow step and that all other steps are so fast that equilibrium may be assumed. The slow step may be either the surface reaction or the adsorption of any one reactant or the desorption of any product. Simplified useful equations may be developed on this basis.

Monomolecular Reactions. Two mechanisms may be postulated for reversible surface reactions which are monomolecular in both directions, such as isomerization reactions. The reaction might proceed through an adsorbed molecule, acquiring sufficient energy to cause it to react and form a product molecule (all the time confined to a single active center). In the other mechanism an adsorbed molecule becomes sufficiently energized to form a complex with an adjacent active center, which then decomposes to form an adsorbed product molecule.

If the first mechanism is followed, the rate of reaction is proportional to the concentration of adsorbed reactant molecules:

$$r = kc_A - k'c_R \tag{33}$$

If the second mechanism is correct, the rate of reaction is proportional to the concentration of pairs of adsorbed molecules and adjacent vacant active centers. This rate is expressed by Equation (27).

If it is assumed that only a single activated step is rate-controlling, simplified over-all equations may be derived according to either mechanism for the reaction:

$$A \rightleftarrows R$$

Surface Reaction Controlling. If the surface reaction is rate-controlling, it is assumed that all adsorption steps are in equilibrium, and the surface concentration terms in Equation (33) may be replaced by Equations (11):

MECHANISM 1

$$r = \frac{kL}{1 + a_{Ai}K_A + a_{Ri}K_R + a_{Ii}K_I + \cdots}\left(a_{Ai}K_A - \frac{a_{Ri}K_R}{K'}\right) \qquad (34)$$

where K' = surface equilibrium constant = k/k'.

At equilibrium the net rate becomes zero, and

$$\frac{a_{Ri}}{a_{Ai}} = \frac{K_A}{K_R}K' = K \qquad (35)$$

Substituting Equation (35) in (34) gives

$$r = \frac{kLK_A}{1 + a_{Ai}K_A + a_{Ri}K_R + a_{Ii}K_I + \cdots}\left(a_{Ai} - \frac{a_{Ri}}{K}\right) \qquad (36)$$

MECHANISM 2. Equation (25) combined with Equations (10) and (11) gives

$$r = \frac{ksLK_A}{(1 + a_{Ai}K_A + a_{Ri}K_R + a_{Ii}K_I + \cdots)^2}\left(a_{Ai} - \frac{a_{Ri}}{K}\right) \qquad (37)$$

The essential difference between Equations (36) and (37) is the squared term in the denominator. According to these equations the initial rate, when $a_{Ri} = 0$, of a reaction following mechanism 1 is progressively increased by increased activity of the reactant in the fluid phase. If mechanism 2 is followed, the initial rate may increase with increased activity of A at low activities, reach a maximum corresponding to an optimum activity, and then diminish as the activity of A is further increased. Effects of this type have been experimentally observed in varying the pressure on monomolecular catalytic reactions.

Adsorption of Reactant Controlling. If the adsorption of the reactant is the rate-controlling step, it is assumed that the surface reaction and the other adsorption steps are in equilibrium. The rate is expressed by the following:

$$r = k_A(a_{Ai}c_l - c_A/K_A) \qquad (38)$$

In the application of Equation (38) all surface concentrations may be expressed in terms of the equilibrium of Equation (7), with the exception of c_A. This surface concentration must be arrived at from the condition of equilibrium in the surface reaction:

$$c_A = \frac{c_R K_A}{K K_R} = \frac{a_{Ri} c_l K_A}{K} \tag{39}$$

$$c_l = L - (c_A + c_R + c_I + \cdots) = L - c_l(a_{Ri}K_A/K + a_{Ri}K_R + a_{Ii}K_I + \cdots)$$

$$c_l = \frac{L}{1 + a_{Ri}K_A/K + a_{Ri}K_R + a_{Ii}K_I + \cdots} \tag{40}$$

Combining Equations (39) and (40) with (38) gives

$$r = \frac{k_A L}{1 + a_{Ri}K_A/K + a_{Ri}K_R + a_{Ii}K_I + \cdots}\left(a_{Ai} - \frac{a_{Ri}}{K}\right) \tag{41}$$

Equation (41) is independent of the mechanism of the surface reaction.

If the form of Equation (41) is compared with (36) and (37), it may be noted that, when adsorption of the reactant is controlling, the initial rate (where $a_{Ri} = 0$) is directly proportional to the activity of the reactant; if the surface reaction is controlling, the initial rate increases less than in proportion to increased activity of the reactant.

Another characteristic of reactions controlled by adsorption is evident by consideration of the net rate of the reverse reaction of Equation (41). If the over-all equilibrium constant K is small, the net rate of the reverse reaction becomes independent of the activity of A. This behavior is characteristic of reactions in which the rate is controlled by the rate of desorption of the product.

Bimolecular–Monomolecular Reactions. The class of reaction which is bimolecular in one direction and monomolecular in the other may be represented by the equation:

$$A + B \rightleftarrows R$$

If it is assumed that the reaction takes place between adjacently adsorbed molecules, it is necessary that the monomolecular reverse reaction follow the mechanism expressed by Equation (25). By the same procedures followed in the preceding section, the following rate equations are developed:

Surface Reaction Controlling

$$r = \frac{k_s L K_A K_B}{(1 + a_{Ai}K_A + a_{Bi}K_B + a_{Ri}K_R + a_{Ii}K_I \cdots)^2} \times \left(a_{Ai}a_{Bi} - \frac{a_{Ri}}{K}\right) \tag{42}$$

Adsorption of A Controlling

$$r = \frac{k_A L}{1 + a_{Bi}K_B + \dfrac{a_{Ri}K_A}{a_{Bi}K} + a_{Ri}K_R + a_{Ii}K_I + \cdots} \times \left(a_{Ai} - \frac{a_{Ri}}{a_{Bi}K}\right) \quad (43)$$

Adsorption of R Controlling

$$r = \frac{k_R L K}{1 + a_{Ai}K_A + a_{Bi}K_B + a_{Ai}a_{Bi}K_R K + a_{Ii}K_I + \cdots} \times \left(a_{Ai}a_{Bi} - \frac{a_{Ri}}{K}\right) \quad (44)$$

In Equation (42) the initial rate of the reaction is increased by increased activity of component B; in Equation (43) increasing the activity of B reduces the initial rate where the activity of R is zero. Thus, it is characteristic of a bimolecular reaction in which the rate is controlled by the adsorption of a reactant that the initial rate is reduced by increased activity of the other reactant.

In Equation (44) the over-all equilibrium constant of the reaction appears in both the numerator and denominator of the multiplying fraction. Under conditions favorable for the forward reaction where K is large, the rate becomes independent of the activity of the product and may approach $k_R L/K_R$, independent of the activities of both reactants and product.

If the reaction on the surface occurs between an adsorbed A molecule and an unadsorbed B molecule in the fluid phase, the rate is proportional to the product of the surface concentration of A and the interfacial fluid activity of B. Equations similar to (42), (43), and (44) result, except that the adsorption-equilibrium constant of B does not appear. If the surface reaction is controlling, the term s does not appear, and the denominator group enters as the first power instead of the square.

Reactions Bimolecular in Both Directions. Reactions of this type are represented by the following equation:

$$A + B \rightleftarrows R + S$$

By extension of the methods demonstrated in the foregoing, the following rate equations may be derived, if the surface reaction is assumed to take place between adjacently adsorbed molecules:

Surface Reaction Controlling

$$r = \frac{ksLK_AK_B}{(1 + a_{Ai}K_A + a_{Bi}K_B + a_{Ri}K_R + a_{Si}K_S + a_{Ii}K_I + \cdots)^2} \times \left(a_{Ai}a_{Bi} - \frac{a_{Ri}a_{Si}}{K}\right) \quad (45)$$

Adsorption of A Controlling

$$r = \frac{k_AL}{1 + \dfrac{a_{Ri}a_{Si}K_A}{a_{Bi}K} + a_{Bi}K_B + a_{Ri}K_R + a_{Si}K_S + a_{Ii}K_I + \cdots} \times \left(a_{Ai} - \frac{a_{Ri}a_{Si}}{a_{Bi}K}\right) \quad (46)$$

Adsorption of R Controlling

$$r = \frac{k_RLK}{1 + a_{Ai}K_A + a_{Bi}K_B + \dfrac{a_{Ai}a_{Bi}K_RK}{a_{Si}} + a_{Si}K_S + a_{Ii}K_I + \cdots} \times \left(\frac{a_{Ai}a_{Bi}}{a_{Si}} - \frac{a_{Ri}}{K}\right) \quad (47)$$

Comparisons between Equations (45), (46), and (47) are similar to those between (42), (43), and (44). A reaction whose rate is controlled by the adsorption of a reactant is characterized by an adverse effect on the initial rate resulting from an increase in activity of the other reactant. A reactant whose rate is controlled by adsorption of a product is characterized by the initial rate being independent of reactant activities under conditions of large over-all equilibrium constants and negligible reverse reaction.

Reactions Involving More than Two Molecules. The adsorption theory of catalysis does not preclude reactions involving the simultaneous interaction of several molecules, and no highly improbable mechanism such as the simultaneous collision of all molecules is involved. The rates of such reactions should be proportional to the concentration of groups of the required number of molecules adsorbed on adjacent active centers. Rate equations might be built up by extension of the procedures used in developing Equations (46) and (47) and the following relations.

It would be expected that the rates of such reactions would be low because of the low concentrations of properly adsorbed groups except in the case of one reactant molecule or atom A reacting with several other molecules or atoms B, all of the same species. In such a case high rates are obtained with a catalyst which strongly absorbs reactant B so that the majority of the surface is covered with adsorbed B molecules or atoms, and most of the A molecules or atoms which are adsorbed are surrounded by the requisite number of B units on adjacent centers.

Effect of Dissociation on Rate Equations. In the development of Equations (29) to (47) it was assumed in every case that all reactants and products are adsorbed without dissociation. From Equation (22) it is evident that, where a molecule dissociates as it is adsorbed, the square root of the product of its activity times its adsorption-equilibrium constant appears in all adsorption-equilibrium expressions in place of the first power of this product. Thus, Equations (36), (37), (42), and (45), in which all adsorption steps are at equilibrium, may be modified to apply where a component is dissociated and one-half molecule participates in the reaction merely by raising to the one-half power the activity and adsorption-equilibrium constant of the component which is dissociated wherever either appears in the equation.

The effects of dissociation where adsorption rate is controlling may be demonstrated by consideration of the effect on Equation (46) of the dissociation of B first and then A. If A is not dissociated the rate is expressed by Equations (4) and (5):

$$r = k_A \left(a_{Ai} c_l - \frac{c_A}{K_A} \right) \tag{48}$$

If B is dissociated and only $\frac{1}{2}B$ molecule enters into the reaction, an expression for c_A is derived from the equilibrium of the surface reaction:

$$c_A = \frac{c_R c_S}{c_{\frac{1}{2}B}^{\frac{1}{2}} K'} = \frac{c_l a_{Ri} K_R a_{Si} K_S}{\sqrt{a_{Bi} K_B} K'} = \frac{c_l a_{Ri} a_{Si} K_A}{\sqrt{a_{Bi}} K} \tag{49}$$

$$c_l = \frac{L}{1 + \dfrac{a_{Ri} a_{Si} K_A}{\sqrt{a_{Bi}} K} + \sqrt{a_{Bi} K_B} + a_{Ri} K_R + a_{Si} K_S + a_{Ii} K_I + \cdots} \tag{50}$$

Substituting Equations (49) and (50) in (48) gives

$$r = \frac{k_A L}{1 + \dfrac{a_{Ri} a_{Si} K_A}{\sqrt{a_{Bi}} K} + \sqrt{a_{Bi} K_B} + a_{Ri} K_R + a_{Si} K_S + a_{Ii} K_I + \cdots} \times \left(a_{Ai} - \frac{a_{Ri} a_{Si}}{\sqrt{a_{Bi}} K} \right) \tag{51}$$

When Equations (51) and (46) are compared, if the component whose adsorption rate is controlling is not dissociated, the rate equations are modified for application where a component is dissociated, and only one-half molecule enters the reaction, by raising the activity and adsorption-equilibrium constant of the dissociated component to one-half power wherever they appear in the equation.

If component A of Equation (46) is dissociated and only one-half molecule enters the reaction, it is necessary to express the rate of reaction by Equation (19). From the equilibrium of the surface reaction,

$$c_{\frac{1}{2}A} = \frac{c_R c_S}{c_B K'} = \frac{c_l a_{Ri} a_{Si} \sqrt{K_A}}{a_{Bi} K} \tag{52}$$

$$c_l = \frac{L}{1 + \dfrac{a_{Ri} a_{Si} \sqrt{K_A}}{a_{Bi} K} + a_{Bi} K_B + a_{Ri} K_R + a_{Si} K_S + a_{Ii} K_I + \cdots} \tag{53}$$

Substituting Equations (52) and (53) in (19), gives

$$r = \frac{sLk_A}{2\left(1 + \dfrac{a_{Ri} a_{Si} \sqrt{K_A}}{a_{Bi} K} + a_{Bi} K_B + a_{Ri} K_R + a_{Si} K_S + a_{Ii} K_I + \cdots\right)^2} \times \left[a_{Ai} - \left(\frac{a_{Ri} a_{Si}}{a_{Bi} K}\right)^2\right] \tag{54}$$

This equation is quite different in form from Equation (46), and it is also dependent on the mechanism assumed for the adsorption and dissociation of A. By assuming a different mechanism (6), an equation can be obtained in which the initial rate is proportional to the one-half power of the activity of A instead of the first power of Equation (54).

If reactant A is dissociated into two chemisorbed half molecules, both of which enter into the reaction, a still different series of equations results. If reactant B is adsorbed without dissociation, the surface reaction in this case involves three active centers. Thus,

$$2(\tfrac{1}{2}A) + B + 3l = R + S + 3l \tag{55}$$

This mechanism, which appears somewhat improbable, requires that the reverse reaction proceed by forming an activated complex involving an R and an S molecule and three active centers. The rate of the surface reaction is proportional to the concentration of adsorbed B molecules with two adsorbed $\frac{1}{2}A$ molecules adjacent to them. An average B molecule is surrounded by s active centers of which a fraction $\theta_{\frac{1}{2}A}$ is occupied by adsorbed $\frac{1}{2}A$ molecules. The average concentration of pairs of adjacently adsorbed B and $\frac{1}{2}A$ molecules is thus $c_B s \theta_{\frac{1}{2}A}$. The B molecule in each of these pairs is in turn surrounded by $(s - 1)$ centers in addition to that occupied by the $\frac{1}{2}A$ molecule. A fraction $\theta_{\frac{1}{2}A}$ of these centers is also occupied by $\frac{1}{2}A$ molecules, and the concentration of B molecules with two $\frac{1}{2}A$ molecules adjacently adsorbed becomes

$$c_{B2(\frac{1}{2}A)} = c_B s \theta_{\frac{1}{2}A}(s - 1)\theta_{\frac{1}{2}A} = \frac{s(s - 1)c_B(c_{\frac{1}{2}A})^2}{L^2} \tag{56}$$

where $\theta_{\frac{1}{2}A}$ = fraction of total centers L which is occupied by $\frac{1}{2}A$ molecules $= c_{\frac{1}{2}A}/L$.

The rate of the surface reaction is expressed by a combination of Equation (56) with a similar expression for the reverse reaction.

$$r = \frac{s(s - 1)k_S}{L^2}\left[c_B(c_{\frac{1}{2}A})^2 - \frac{c_R c_S c_l}{K'}\right] \tag{57}$$

If equilibrium is maintained in the adsorption steps, Equations (10), (11), and (22) may be combined with (57):

$$r = \frac{s(s - 1)Lk_S K_A K_B}{(1 + \sqrt{a_{Ai}K_A} + a_{Bi}K_B + a_{Ri}K_R + a_{Si}K_S + a_{Ii}K_I)^3} \left(a_{Ai}a_{Bi} - \frac{a_{Ri}a_{Si}}{K}\right) \tag{58}$$

Equations may similarly be derived for cases in which this mechanism is followed by an adsorption rate as the controlling step. If the adsorption of A is controlling, the rate is expressed by Equations (19) and (20):

$$r = \frac{sk_A}{2L}\left[a_{Ai}c_l^2 - \frac{(c_{\frac{1}{2}A})^2}{K_A}\right] \tag{59}$$

Since the surface reaction and the adsorption of B, R, and S are assumed to maintain equilibrium,

$$(c_{\frac{1}{2}A})^2 = \frac{c_R c_S c_l}{c_B K'} = \frac{a_{Ri}a_{Si}c_l^2 K_R K_S}{a_{Bi}K_B K'} = \frac{a_{Ri}a_{Si}c_l^2 K_A}{a_{Bi}K} \tag{60}$$

$$c_l = L - c_l\left[\sqrt{\frac{a_{Ri}a_{Si}K_A}{a_{Bi}K}} + a_{Bi}K_B + a_{Ri}K_R + a_{Si}K_S + a_{Ii}K_I\right]$$

or

$$c_l = \frac{L}{\left[1 + \sqrt{\frac{a_{Ri}a_{Si}K_A}{a_{Bi}K}} + a_{Bi}K_B + a_{Ri}K_R + a_{Si}K_S + a_{Ii}K_I\right]} \tag{61}$$

Substituting (60) and (61) in (59), gives

$$r = \frac{s k_A L}{2\left[1 + \sqrt{\frac{a_{Ri} a_{Si} K_A}{a_{Bi} K}} + a_{Bi} K_B + a_{Ri} K_R + a_{Si} K_S + a_{Ii} K_I\right]^2} \left(a_{Ai} - \frac{a_{Ri} a_{Si}}{a_{Bi} K}\right) \qquad (62)$$

If the adsorption of B, R, or S is controlling, the rate equations are similar in form to Equations (46) and (47), except that in the denominator group the product of the activity times the adsorption-equilibrium constant of the dissociated molecules is raised to the one-half power.

POISONS

The term "poison" has been loosely used to denote any material which retards the rate of a catalytic reaction. Thus, the products of the reaction are sometimes referred to as poisons because increasing their concentration reduces the rate. However, it is believed more logical to eliminate all reactants and products from classification as poisons and reserve the term for other components which retard the reaction by reducing the number of active centers available for the reactants. Such poisons may be classified as either temporary or permanent.

From inspection of the rate equations it is evident that any inert component I which is adsorbed on the active centers promoting the reaction serves as a poison; the extent of the retardation depends on the concentration of the inert and its adsorption-equilibrium constant. If the adsorption of the inert is reversible with a moderate equilibrium constant, the poisoning effect quickly reaches a constant value which is temporary and is eliminated by removal of the component from the reactant fluid. Thus, the nitrogen in air might serve as a temporary poison in a catalytic oxidation. The effects of such inerts are included in the rate equations.

Another type of poisoning frequently encountered results from the permanent substantially irreversible adsorption of components present in small quantities in the reactant fluid. The effect of this type of poisoning is progressively to reduce L', the number of active centers per unit area, as the catalyst continues in service. The frequently observed loss of activity of a catalyst in service may result from poisoning of this type, from structural changes affecting the area and L, or from physically coating the active surface with a solid or semisolid material either present in the reactants or formed by secondary reactions. In high-temperature organic reactions, catalysts are frequently coated with high-molecular-weight compounds approaching pure carbon in composition.

Limitations of Surface Rate Equations. The rate equations derived in the foregoing are ideal forms involving several assumptions which are not rigorous. The derivation implies that all active centers on the catalytic surface behave similarly, but there is evidence that this is not the case. Frequently the energy of activation gradually increases as active centers are progressively occupied. It is well known that surface activity depends upon spatial arrangement of active centers which may not be uniform over the entire surface. Also it is assumed that each component is adsorbed independent of interaction between the adsorbed molecules of like or unlike species. Again there is evidence that such is not the case, and corrections are developed[6] for such interaction effects in simple systems.

Although numerous attempts have been made to establish more rigorous adsorption relations, there is little evidence that their use is justified in rate equations for complex reaction systems. It is believed more generally satisfactory to use the equations previously developed and evaluate the constants from direct-reaction rate measurements at conditions representing the ranges of interest of the variables. Constants directly evaluated from experimental data in this manner represent average apparent or effective values over the range considered, and the resultant equations cannot be expected to be entirely rigorous.

As in all theoretical rate calculations, the form of the relation is dependent on the mechanism. This situation is entirely different from that encountered in thermodynamic equilibrium calculations in which the mechanism is immaterial. Furthermore, the correct mechanism cannot be selected by consideration of stoichiometric equations but must be determined by comparison of the trends of experimental data with the trends manifested in the various rate equations.

Conversion Equations. In a steady-state flow system the relationship between space velocity and conversion is obtained by consideration of an elementary section of reactor containing a mass of catalyst dW in which a conversion dx is produced. Then

$$F\,dx = r\,dW \tag{63}$$

where F = feed rate, mass per unit time
W = mass of catalyst in reactor
r = reaction rate, moles/(mass of catalyst)(time)
x = conversion, moles per unit mass of feed

Integration yields

$$\frac{W}{F} = \frac{1}{S_v}\frac{\rho_B}{\rho_f} = \int_0^x \frac{dx}{r} \tag{64}$$

where S_v = space velocity, volume of feed/(volume of catalyst bed)(time)
ρ_B = bulk density of catalyst, mass/volume
ρ_f = density of feed, mass/volume

The integration of Equation (64) can be completed only when r is expressed as a unique function of x. In all except the most simple cases of reactions at constant temperature and pressure this integration is best carried out graphically by plotting x against $1/r$. Where temperature and pressure vary throughout the reactor, a step-by-step procedure similar to that of Illustration 13, Chapter XVIII, page 875, must be employed.

Useful integrated equations may be developed from (64) for simple reactions in which diffusional effects are negligible and temperature and pressure are constant. For example, Equation (36) represents the rate of a reversible reaction which is monomolecular in both directions and is controlled by a surface reaction involving single active centers. For a feed composed of pure reactant A, if diffusional effects are negligible and activities are equal to partial pressures,

$$a_{Ai} = (1 - x)\pi$$
$$a_{Ri} = x\pi$$

where x = moles of A converted per mole of feed
π = total pressure

Substituting in Equation (36) and combining with (64) gives

$$\frac{W}{F} = \frac{1}{C}\int_0^x \frac{[1 + (1 - x)\pi K_A + x\pi K_R]\,dx}{\pi\left[(1 - x) - \dfrac{x}{K}\right]} \tag{65}$$

where $C = kLK_A$, a constant at constant temperature
Rearranging gives

$$\frac{W}{F} = \frac{1}{C}\int_0^x \frac{[(1/\pi + K_A) + (K_R - K_A)x]\,dx}{[1 - (1 + 1/K)x]} \tag{66}$$

Integration gives

$$\frac{W}{F} = \left[\frac{(1/\pi + K_A)(1 + 1/K) + (K_R - K_A)}{C(1 + 1/K)^2}\right]\left[\ln\frac{1}{1 - \left(1 + \dfrac{1}{K}\right)x}\right] - \frac{(K_R - K_A)x}{C\left(1 + \dfrac{1}{K}\right)} \tag{67}$$

Equation (67) contains three constants, C, K_A, and K_R, in addition to the over-all thermodynamic equilibrium constant K. All constants are assumed to be functions of temperature only for a given system. Once these constants are evaluated, a complete relationship is obtained among conversion, space velocity, and pressure, at conditions of constant temperature and pressure.

In Table LVII are conversion equations for a few simple reactions in which diffusional effects are negligible. Similar equations for other cases may be developed by the general procedure followed in deriving Equation (67). Such equations are useful primarily for the interpretation of laboratory data in which conditions of constant temperature and pressure may be closely approximated. Many of the equations involve differences between logarithmic terms which require a high order of numerical accuracy for satisfactory computations. For this reason graphical integration of Equation (64) is frequently more convenient than use of an integrated equation even where the latter is available and applicable.

TABLE LVII

CATALYTIC CONVERSION EQUATIONS

Assuming: Ideal-gas behavior
No reaction products in the feed
Surface reaction controlling

Nomenclature at end of table

$\boldsymbol{A \rightleftarrows R}$; x = moles A reacted per mole of feed

Single-Site Mechanism:

$$\left.\begin{aligned} &C\left(\frac{W}{F}\right) = \frac{\alpha a + \beta n_{A0}}{a^2} \ln\left(\frac{n_{A0}}{n_{A0} - ax}\right) - \frac{\beta x}{a} \\ &a = (1 + 1/K); \qquad \alpha = (1/\pi + K_A n_{A0} + K_I n_I); \qquad \beta = (K_R - K_A) \end{aligned}\right\} \qquad \text{(a)}$$

Dual-Site Mechanism:

$$\frac{C}{\pi}\left(\frac{W}{F}\right) = \left(\frac{\alpha^2}{a} + \frac{2\alpha\beta n_{A0}}{a^2} + \frac{\beta^2 n_{A0}^2}{a^3}\right)\left(\ln \frac{n_{A0}}{n_{A0} - ax}\right) - \frac{2\alpha\beta x}{a} - \frac{\beta^2 x^2}{2a} - \frac{\beta^2 n_{A0} x}{a^2} \qquad \text{(b)}$$

where

$$a = 1 + 1/K; \qquad \alpha = (1/\pi + K_A n_{A0} + K_I n_I); \qquad \beta = (K_R - K_A)$$

$\boldsymbol{A \rightleftarrows R + S}$; x = moles A reacted per mole of feed

Dual-Site Mechanism with a feed of pure A; $n_{A0} = 1.0$

$$\left.\begin{aligned} &\frac{C}{\pi}\left(\frac{W}{F}\right) = \frac{1}{2\sqrt{a}}\left(\alpha^2 + \frac{\beta^2}{a}\right) \ln \frac{1 + x\sqrt{a}}{1 - x\sqrt{a}} - \frac{\alpha\beta}{a} \ln\,(1 - ax^2) - \frac{\beta^2 x}{a} \\ &\text{where} \\ &a = 1 + \pi/K; \quad \alpha = (1/\pi + K_A); \quad \beta = (1/\pi + K_R + K_S - K_A) \end{aligned}\right\} \qquad \text{(c)}$$

Dual-Site Mechanism with a diluent I present in such large proportions that the change in the number of total moles is negligible:

$$\frac{C}{\pi}\left(\frac{W}{F}\right) = \left(\frac{\beta^2}{2a^2} - \frac{\alpha\beta}{a}\right) \ln \left(\frac{n_{A0} - x - ax^2}{n_{A0}}\right) - \frac{\beta^2 x}{a} + \left(\frac{\beta^2(1 + 2n_{A0}a)}{2a^2} - \frac{\alpha\beta}{a} + \alpha^2\right)\frac{1}{\gamma} \ln \frac{(2ax + 1 + \gamma)(1 - \gamma)}{(2ax + 1 - \gamma)(1 + \gamma)} \tag{d}$$

where

$$a = \pi/K; \qquad \alpha = (1/\pi + K_A n_{A0} + K_I m_I)$$

$$\beta = (K_R + K_S - K_A); \qquad \gamma = \sqrt{4n_{A0}a + 1}$$

$A + B \rightleftarrows 2R$

Dual-Site Mechanism; equimolal proportions of A and B in feed:

x = moles of R formed per mole of feed
n_0 = moles of $A + B$ originally present per mole of feed

$$\frac{C}{4}\left(\frac{W}{F}\right) = \frac{\beta^2 x}{a} + \left(\frac{\alpha\beta}{a} + \frac{\beta^2 n_0}{a^2}\right) \ln \frac{(ax^2 - 2n_0 x + n_0^2)}{n_0^2} + \frac{1}{2\gamma}\left[\alpha^2 + \frac{2\alpha\beta n_0}{a} + \frac{\beta^2 n_0^2(2 - a)}{a^2}\right] \ln \frac{(ax - n_0 - \gamma)(-n_0 + \gamma)}{(ax - n_0 + \gamma)(-n_0 - \gamma)} \tag{e}$$

$$a = (1 - 4/K); \qquad \alpha = 1/\pi + (K_A + K_B)n_0/2 + K_I n_I$$

$$\beta = [K_R - (K_A + K_B)/2]; \qquad \gamma = \sqrt{n_0^2 - an_0^2}$$

Nomenclature

a = constant, defined for each equation
C = combined proportionality factor in the differential rate equation written in terms of activities referred to unit fugacity
F = feed rate, moles per unit time
K = over-all thermodynamic equilibrium constant of the gas-phase reaction
K_A, K_B, etc. = adsorption-equilibrium constants of components A, B, etc.
n_{A0} = moles of A originally present per mole of feed
n_I = moles of inert component I, per mole of feed
W = mass of catalyst in the reactor
α, β, γ = constants, defined for each equation
π = total pressure in units used for expressing fugacity in the differential rate equation

CATALYST FOULING AND DEACTIVATION

In many high-temperature organic reactions in the presence of a solid catalyst the conversion rapidly declines owing to the accumulation of a carbonaceous *catalyst deposit* as processing is continued under constant operating conditions. Frequently this fouling of the catalyst and the necessity of removing the deposit causing it constitute the most serious problems encountered in the design of a process. Three fundamentally different solutions to this problem are in commercial use:

1. Two or more alternate reactors are provided to permit continuous operation in one while another is being regenerated by removal of catalyst deposit. Regeneration is most commonly accomplished by oxidation. In this case removal of the heat liberated becomes a major problem which may be handled by:

(*a*) Use of a reactivation gas containing so small a quantity of oxygen that the heat of combustion may be removed with but a small rise in temperature. This scheme normally involves recirculation of hot oxygen-free combustion gases to which a small quantity of air is added.

(*b*) Indirect cooling of the catalyst bed by circulating a gaseous or liquid heat-transfer medium. This requires that the catalyst be contained in a specially designed reactor with extensive heat-transfer surface.

(*c*) Storage of the heat liberated in regeneration in the catalyst bed for use in the subsequent processing period. This so-called " regenerative adiabatic " operation is feasible only if the catalytic reaction is endothermic and an exact balance can be maintained between the heat evolved in regeneration and that absorbed in processing.

Equipment for the operation of alternating reactors with process periods as short as 5 min has been highly developed in the Houdry Process for the catalytic cracking of petroleum[8] in processes for the dehydrogenation of butane and butenes and other high-temperature reactions.

2. The catalyst may be continuously removed from the reactor and transferred to a regenerator where the deposit is burned. This principle is employed in the TCC catalytic cracking process[9] in which catalyst pellets are mechanically transferred from the reactor to a kiln in which the deposit is burned. It is also followed in the " Fluid " catalytic cracking process[10] which employs finely divided catalyst suspended in a " fluidized " state in the hydrocarbons being cracked and in the air used for regeneration. In such " moving-bed " operations the time during which the catalyst is in the reactor as determined by the rate of catalyst circulation is analogous to the length of the process period in an operation employing a fixed catalyst bed.

3. The catalyst deposit may be continuously removed by addition of a regenerating constituent to the reactant stream. This method has been successfully used in dehydrogenating butene to butadiene. In this

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[8] R. H. Newton and H. G. Shimp, *Trans. Am. Inst. Chem. Engrs.*, **41**, 197 (1945).

[9] R. H. Newton, G. S. Dunham, and T. P. Simpson, *Trans. Am. Inst. Chem. Engrs.*, **41**, 215 (1945).

[10] E. V. Murphree, C. L. Brown, F. J. Gohr, C. E. Jahnig, H. Z. Martin, and C. W. Tyson, *Trans. Am. Inst. Chem. Engrs*, **41**, 19 (1945).

process[11] steam is the regenerating agent and removes carbonaceous material by the familiar water-gas reaction, producing a mixture of CO, CO_2, and hydrogen.

Quite different from the relatively rapid fouling of a catalyst by carbonaceous deposits is its progressive *deactivation* with continued use. This phenomenon of long-time deactivation is encountered either with or without short-time fouling. Thus, each regeneration to remove catalyst deposit may restore the catalyst to a slightly lower activity than the preceding one. Such progressive loss in activity may result from irreversible poisoning, from structural changes of the catalyst, or from gradual loss of some constituent of the catalyst. Continued service at high temperature is known to reduce the surface area of some catalysts and also to produce changes in lattice structure which are evidenced by changed diffraction patterns. In many cases it appears that these structural changes are accelerated both by increased temperature and by contact with water vapor. The effect of water vapor in promoting such rearrangements of solid inorganic catalysts is particularly marked at temperatures of 1000°F or higher.

It is common practice to compensate for deactivation of a catalyst by progressively increasing the temperature or pressure of the reaction. Loss of production may be avoided in this manner for a time, but eventually the activity of the catalyst reaches a level at which further operation is uneconomical, and it must be either replaced by new catalyst or subjected to some *reactivation* operation. Reactivation may involve chemical treatment to remove poisons or to restore some lost constituent, or may consist of alternate oxidation and reduction or solution and precipitation to restore the surface structure of the catalyst.

Considerable confusion exists in the use of the terms " regeneration " and " reactivation." It is believed preferable to designate the removal of catalyst deposit formed by short-time fouling as regeneration to distinguish this operation from the periodic restoration of catalyst activity by reactivation.

Fouling Factors. The effect of fouling on the results produced by a catalyst is best studied by plotting the duration of processing time against the conversion produced at fixed operation conditions. The conversion plotted may be either the differential or instantaneous conversion being produced at the time in question or the integral or average conversion from the beginning of the process period to the time in question. The former type of curve may be established experimentally from a single long process period by analysis of a series of " spot " samples taken at intervals. The latter type of curve is established by analyzing the total product from a number of process periods of different length. Once either curve is established the other can be derived by graphical integration or differentiation.

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[11] R. P. Russell, E. V. Murphree, and W. C. Asbury, *Trans. Am. Inst. Chem. Engrs.*, **42**, 1–14 (1946).

In Fig. 182 are curves from the data of Johanson and Watson[12] relating both instantaneous and average conversions to process-period length for the production of toluene from an equimolal mixture of benzene and

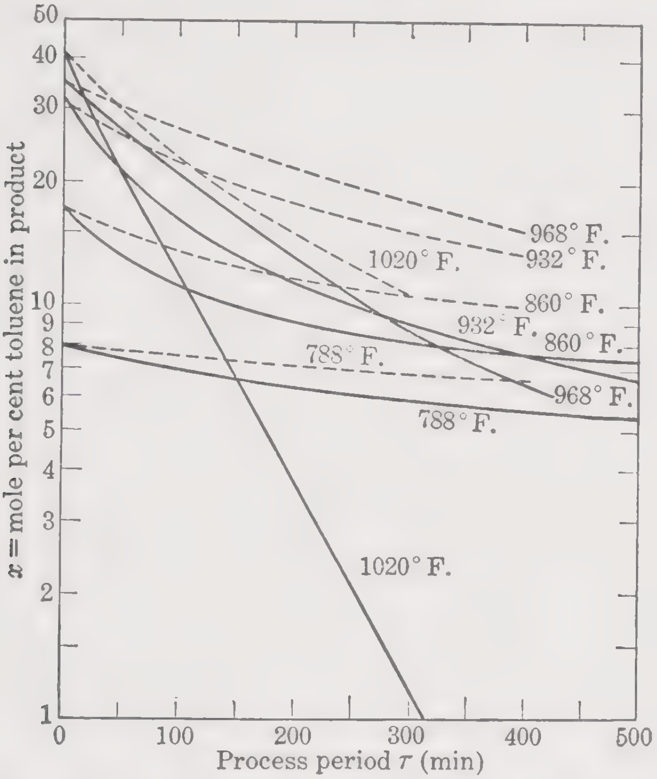

FIG. 182. Effect of Process Period upon the Production of Toluene. (Pressure = 31.5 atmospheres: $W/F = 66$.)

xylene passed at a liquid hourly space velocity of 1.0 over a silica–alumina cracking catalyst at a gauge pressure of 450 lb per sq in. and at the various indicated temperatures. The instantaneous conversions were determined and the average conversions calculated.

It may be noted that the rate of fouling of the catalyst, as indicated by the slope of the curves of Fig. 182, increases rapidly with increased temperature. Thus, although for short process periods conversion increases progressively with increased temperature, with longer process periods the conversion at 1020°F drops below that obtained at much lower temperatures.

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[12] L. N. Johanson and K. M. Watson, Natl. Petroleum News, Tech. Sec. (August and September 1946). Also "Principles of Reactor Design," National Petroleum Publishing Company, Cleveland (1946).

It is evident that the complete rate equation for a catalyst which undergoes fouling and periodic regeneration must include the effect of process-period length, or apparent catalyst residence time in the case of moving-bed operations. There are not sufficient data available on any one system to establish with certainty the best procedure for introducing such a factor into a fundamental rate equation. A "fouling factor" might be introduced as a multiplying factor in the numerator of the rate equation with the philosophy that fouling merely reduces L, the total number of active centers on the catalyst surface. An alternate procedure is to introduce the fouling factor as an added term in the group in the denominator of the rate equation with the view that fouling has the same effect as the equilibrium adsorption of a constituent on the active centers. In either case the fouling factor would be a function of temperature, pressure, conversion, and process-period length.

Johanson and Watson obtained fair correlation of their data with a rate equation in which a fouling factor was introduced in the latter form. The principal reaction under consideration was as follows:

$$C_6H_6 + C_6H_4(CH_3)_2 \rightleftarrows 2C_6H_5CH_3 \tag{68}$$

There is evidence that toluene is also simultaneously produced by disproportionation of xylene to form trimethyl benzene and toluene. However, for the restricted case of a feed of equimolal proportions Johanson and Watson assumed that the over-all rate of production of toluene could be expressed by the empirical evaluation of the rate equation of reaction (68). On this basis it was found that the average conversion data over wide ranges of conditions were fairly well represented by the following basic rate equation:

$$r = \frac{C(a_A a_B - a_R^2/K)}{(1 + a_A K_A + a_B K_B + a_R K_R + B\pi)^2} \tag{69}$$

where subscripts A, B, R refer to benzene, xylene, and toluene, respectively, and

$B\pi$ = the fouling factor = $\pi(u\tau^b + v\tau^c x)$ (70)
τ = process-period length
u, v = functions of temperature
b, c = constants
x = average conversion, moles of toluene per mole of feed of equimolal composition produced from the beginning of the process period to time τ

In Figs. 183, 184, and 185 are average conversions calculated by integration of Equation (69) to show the effects of varying pressure, space velocity, and temperature, respectively, at process-period lengths τ of 0, 50, and 300 min. It may be noted that the length of the process period is an important variable which must be carefully considered in the engineering analysis of such a process.

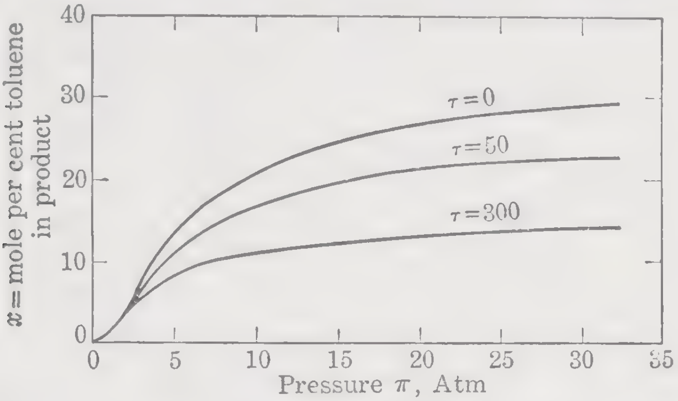

FIG. 183. Effect of Pressure on the Production of Toluene from an Equimolal Mixture of Benzene and Xylene. ($W/F = 66$; temperature = 932° F.)

The methods followed in evaluating the constants of Equation (69) are discussed on page 938.

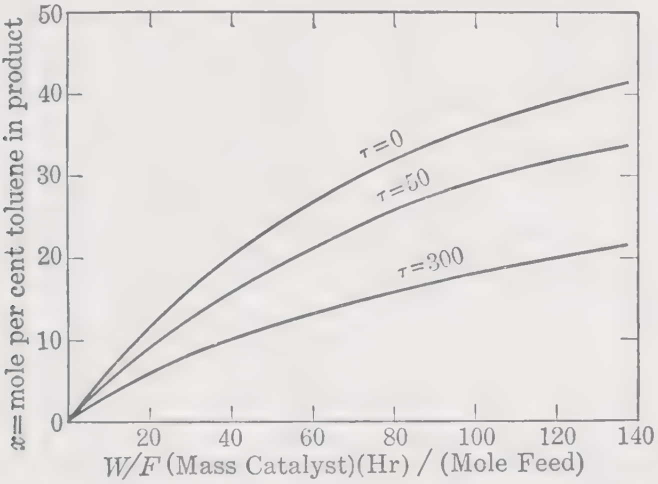

FIG. 184. Effect of Catalyst–Feed-Rate Ratio on the Production of Toluene. (Temperature = 932° F; pressure = 31.5 atm.)

Activity Factors. The constants in catalytic rate equations are strictly applicable only to the catalyst for which they were evaluated and are rendered invalid by any changes in catalyst activity. In some cases a change in the catalyst due either to changed preparation or to deactivation in use may markedly change both the adsorption-equilibrium constants and the over-all rate factor. In this event all constants must be re-evaluated at different levels of catalyst activity in order to maintain a valid rate equation. However, where changes in catalyst activity are not too great it is frequently possible to take them into account merely by including a *catalyst-activity factor* in the over-all rate factor of the equation. For example, Equation (69) might be written:

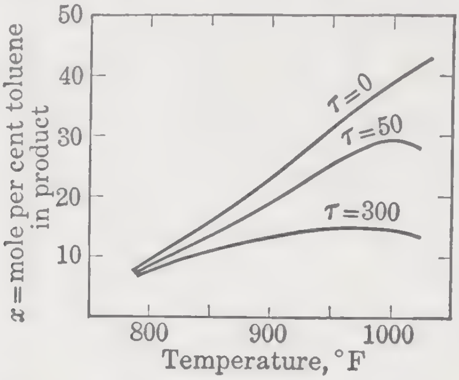

FIG. 185. Effect of Temperature on the Production of Toluene. (W/F = 66; pressure = 31.5 atm.)

$$r = \frac{L_r C'(a_A a_B - a_R^2/K)}{(1 + a_A K_A + a_B K_B + a_R K_R + B\pi)^2} \tag{71}$$

where L_r = the catalyst-activity factor, a constant depending only on catalyst activity

It is evident that the factor L_r will appear as a multiplier in any integrated-conversion equation of the type shown in Table LVII. Thus, if the same conversion is produced by catalysts of different activities they must operate at different space velocities, and, under these conditions,

$$\frac{L_{r2}}{L_{r1}} = \left[\frac{(W/F)_1}{(W/F)_2}\right]_x \tag{72}$$

If catalyst 1 of Equation (72) is adopted as an arbitrary standard of comparison and assigned an activity factor of 1.0, the activity factor of any other catalyst of generally similar type may be determined by experimentally evaluating the conversion produced at a selected space velocity. If the conversion produced by the standard catalyst at the same conditions is known, the activity factor is calculated directly from Equation (72).

Ordinarily catalyst activities are compared at standardized test conditions. Frequently activity ratings have been based on merely a ratio of the conversions obtained in such a test. Such a scale may give a distorted picture of the relative activities as indicated by Fig. 186 in which conversion x is plotted against W/F for a standard catalyst. A catalyst producing a conversion represented by point B has an activity factor equal to the ratio of the abscissa at point C to that at B. Similarly, a catalyst producing the conversion indicated by D has an activity factor equal to the ratio of abscissas E/D. Such factors are much more descriptive of the change in properties of the catalyst than would be ratios of the ordinates B/A and D/A, and they may be used directly in rate and conversion equations in ranges where the adsorption-equilibrium constants are not seriously changed. The only additional work involved in expressing activities on this basis is the evaluation of the relationship between x and W/F for the standard catalyst.

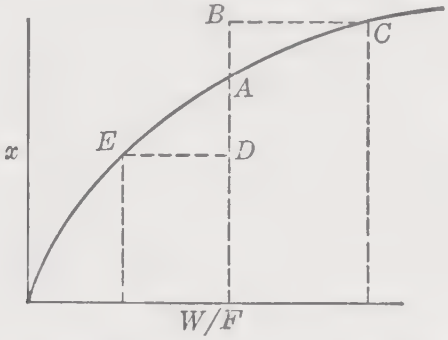

FIG. 186. Catalyst Activity Factors.

EVALUATION OF RATE EQUATIONS

Each of the equilibrium and velocity constants of the rate equations is a function of temperature in accordance with the following equations discussed in Chapters XVI and XVIII.

$$K = e^{-\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}} \tag{73}$$

$$k = \frac{\mathbf{k}T}{\mathbf{h}\alpha^{\ddagger}} e^{\frac{-\Delta H^{\ddagger}}{RT} + \frac{\Delta S^{\ddagger}}{R}} \tag{74}$$

where $\gamma^{\ddagger}$ = activity coefficient of the activated complex = $a^{\ddagger}/c^{\ddagger}$
$c^{\ddagger}$ = concentration of the activated complex, moles per unit mass.

The incorporation of (74) in a rate equation is simplified by combining all the multiplying constants into an over-all rate constant C. Thus, for Equation (45),

$$C = \frac{\mathbf{k}TsLe^{-\frac{\Delta H^{\ddagger} + \Delta H_A^{\circ} + \Delta H_B^{\circ}}{RT} + \frac{\Delta S^{\ddagger} + \Delta S_A^{\circ} + \Delta S_B^{\circ}}{R}}}{\gamma^{\ddagger}\mathbf{h}} = Te^{-\frac{b}{RT} + A} \tag{75}$$

and assuming $\gamma^{\ddagger}$ to be constant, this equation may be written

$$r = \frac{Te^{-\frac{b}{RT}+A}}{(1 + a_{Ai}K_A + a_{Bi}K_B + a_{Ri}K_R + a_{Si}K_S + a_{Ii}K_I + \cdots)^2} \left(a_{Ai}a_{Bi} - \frac{a_{Ri}a_{Si}}{K}\right) \tag{75a}$$

It is evident from consideration of Equations (73) to (75a) that each of the constants in the catalytic rate equations can be expressed as a function of temperature by evaluating it at two different temperatures. Thus, in order to establish completely the kinetic behavior of a system, sufficient rate data must be obtained to permit evaluation of each constant of the fundamental rate equation at two temperatures. Furthermore, the data must be sufficient to establish the mechanism of the reaction and to identify the rate-controlling step in order that the proper equation form may be used.

In order that the constants of a rate equation may be evaluated at a selected temperature, it is necessary that rate data shall be available which include at least two different values of each variable so that a number of *independent* equations may be established which is equal to the number of unknown constants. These equations are then solved simultaneously to determine the constants. Ordinarily, more than this theoretical minimum of data is required in order to establish the correct mechanism and equation form.

Evaluation of Constants by Least Squares. In developing the constants of an equation to represent experimentally observed data it is desired to arrive at the most probable or " best " relationship which will represent all of the data with a minimum average error or deviation. Where errors are small and only a single unknown constant is involved, it is generally satisfactory to calculate the constant from each of the available experimental observations and to adopt the arithmetic average value. Where large deviations are encountered, this procedure does not lead to the most probable solution. Furthermore, it is not applicable to the simultaneous evaluation of several constants.

The mathematical theory of probability has resulted in the development of the Gaussian law of error which leads to the conclusion that the most probable value of a quantity which is derived from a number of experimental observations of *equal absolute precision* is that value from which the sum of the *squares* of the deviations of the individual measurements is a minimum. The derivation of this "principle of least squares" may be found in standard mathematical texts which deal with probability.

The principle of least squares is particularly valuable for evaluating equations which can be written in such a form which is linear with respect to each unknown constant. This general form is

$$y = a + bx_b + cx_c + \cdots \tag{76}$$

where $y, x_b, x_c, \cdots =$ experimentally determined quantities which do not involve unknown constants

$a, b, c, \cdots =$ unknown constants

The deviation D of any observed value of y from the most probable value calculated from the corresponding values of $x_b, x_c, \cdots$ is expressed by

$$D = a + bx_b + cx_c + \cdots - y \tag{77}$$

According to the principle of least squares the most probable values of $a, b, c, \cdots$ are those which result in a minimum value of ΣD^2 for all of the n experimental observations involved. Thus,

$$\Sigma D^2 = D_1^2 + D_2^2 + \cdots + D_n^2 = \text{minimum} \tag{78}$$

Since ΣD^2 is a function of the unknowns $a, b, c \cdots$ its minimum corresponds to a zero value for the derivative of ΣD^2 with respect to each of the unknowns. Thus, with respect to a,

$$\frac{\partial(\Sigma D^2)}{\partial a} = 2\left[D_1\frac{\partial D_1}{\partial a} + D_2\frac{\partial D_2}{\partial a} + \cdots + D_n\frac{\partial D_n}{\partial a}\right] = 0 \tag{79}$$

Similar expressions may be written with respect to each of the other unknowns. The terms $\partial D/\partial a$, $\partial D/\partial b$, etc., may be evaluated from Equation (77). Thus, $\partial D/\partial a = 1$, and

$$\begin{aligned}\frac{\partial(\Sigma D^2)}{\partial a} &= 2(a + bx_{b1} + cx_{c1} + \cdots - y_1 \\ &\qquad + \cdots + a + bx_{bn} + cx_{cn} + \cdots - y_n) = 0\end{aligned} \tag{80}$$

Similarly, since $\partial D/\partial b = x_b$,

$$\begin{aligned}\frac{\partial(\Sigma D^2)}{\partial a} &= 2(ax_{b1} + bx_{b1}^2 + cx_{c1}x_{b1} + \cdots - x_{b1}y_1 \\ &\qquad + \cdots + ax_{bn} + bx_{bn}^2 + cx_{cn}x_{bn} + \cdots - x_{bn}y_n) = 0\end{aligned} \tag{81}$$

Similar equations may be written with respect to c and any other unknown constants in the basic equation. These equations may be written in summation form as follows:

$$na + b\Sigma x_b + c\Sigma x_c + \cdots - \Sigma y = 0 \tag{82}$$

$$a\Sigma x_b + b\Sigma x_b^2 + c\,\Sigma x_c x_b + \cdots - \Sigma y x_b = 0 \tag{83}$$

$$a\Sigma x_c + b\Sigma x_b x_c + c\,\Sigma x_c^2 + \cdots - \Sigma y x_c = 0 \tag{84}$$

Each of the summations of Equations (82–84) may be evaluated from the n experimental values of x_b, x_c, $\cdots$ and y. Thus three equations are obtained which may be solved simultaneously for the most probable values of the three unknowns, a, b, and c. If more constants are involved, additional equations may be developed by the same procedure.

Illustration 1. In the life test of a catalyst weekly determinations are made of the activity factor L_r. These data for a period of 9 weeks are shown in Table A and plotted in Fig. 187. Assuming a linear relationship between the activity factor and time, estimate its value after 180 days of service.

TABLE A

Observation	*Service Time,* days, τ	*Activity Factor,* L_r	τ^2	τL_r
1	0	39	0	0
2	7	40	49	280
3	14	38	196	532
4	21	38	441	798
5	28	35	784	980
6	35	38	1225	1330
7	42	37	1764	1554
8	49	35	2401	1715
9	56	37	3136	2072
Σ	252	337	9996	9261

The relationship assumed is $L_r = a + b\tau$. Thus, in applying Equations (82–84), $y = L_r$ and $x_b = \tau$ while the other variables are all zero. The two equations required for evaluation of a and b follow from (82) and (83).

$$na + b\Sigma\tau - \Sigma L_r = 0 \tag{a}$$

$$a\Sigma\tau + b\Sigma\tau^2 - \Sigma\tau L_r = 0 \tag{b}$$

The summation in Equations (a) and (b) are evaluated in Table A. With these substitutions, since $n = 9$,

$$9a + 252b - 337 = 0 \tag{c}$$

$$252a + 9996b - 9261 = 0 \tag{d}$$

Multiplying (c) by 252/9 to eliminate a, we get

$$252a + 7056b - 9436 = 0 \tag{e}$$

Combining (d) and (e) gives

$$2940b = -175 \qquad 05952$$

From (c), $a = (337 + 15.00)/9 = 39.11$

The most probable equation is therefore $L_r = 39.11 - 0.05952\tau$, and, when $\tau = 180$, $L_r = 39.11 - 10.71 = 28.40$. The curve in Fig. 187 is a plot of this equation.

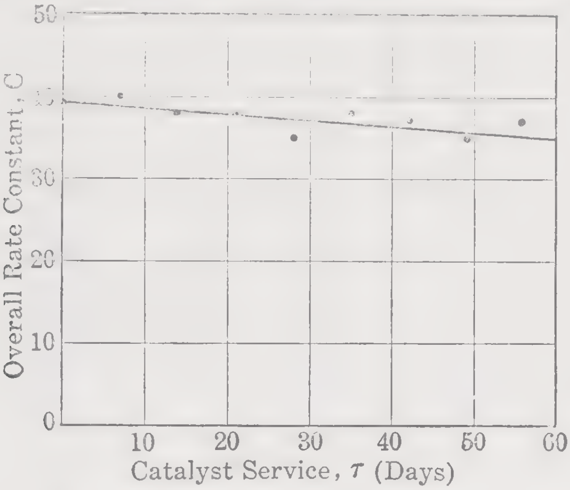

FIG. 187. Most Probable Life of Catalyst.

If more extensive life data were available, a better basis for prediction would be a three-term equation of the form $L_r = a + b\tau + c\tau^2$. The constants of this equation could be determined by simultaneous solution of three equations developed from (82–84).

Use of the method of least squares requires a high order of numerical accuracy in the calculations. Where three constants are involved, these are most conveniently evaluated by determinants.

It may be noted that, although Equation (76) is linear with respect to the constants $a, b, c, \cdots$, the variable terms $y, x_b, x_c, \cdots$ may be complex functions of any form. For example, the initial rate of a unimolecular reaction controlled by a dual site with surface reaction in a pure feed containing only reactant A is expressed by the following equation:

$$r_0 = \frac{C\pi}{(1 + K_A\pi)^2} \tag{85}$$

$$\sqrt{\frac{\pi}{r_0}} = \frac{1}{\sqrt{C}} + \frac{K_A}{\sqrt{C}}\pi \tag{86}$$

In this equation $y = \sqrt{\pi/r_0}$; $a = 1/\sqrt{C}$; $b = K_A/\sqrt{C}$, and $x_b = \pi$. The constants may be evaluated from experimental data for r_0 and π by the procedure of Illustration 1. Similarly, Equation (73) may be rewritten in a form which is linear with respect to the unknown constants ΔH° and ΔS°. Thus,

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{87}$$

In this case $y = \ln K$; $a = \Delta S^\circ/R$; $b = \dfrac{-\Delta H^\circ}{R}$, and $x_b = 1/T$. The method of least squares is readily applicable to determination of ΔS° and ΔH° from data for K and T. In all such rearrangements it is necessary that the form of Equation (76) be obtained with y, a dependent variable or group of variables which contains no unknown constant.

It is evident that the method of least squares may be applied to the evaluation of constants in relationships of many different forms. However, it should be remembered that the basic assumption of the method is that the absolute precision of measurements is constant over the entire range. Thus, in applying the method to Equation (86) it is assumed that the precision of determination of $\sqrt{\pi/r_0}$ is constant, while for Equation (87) it is assumed that the *absolute* error of measurement of $\ln K$ is constant. This latter assumption corresponds to a constant *percentage* error in the measurement of K. The method of least squares is not rigorous where the methods of measurement are such that this fundamental assumption is not correct.

The method of least squares may be used to determine the best constants in a given form of equation and also for establishing the best form of equation for a given set of data. The best constants are first evaluated for each form of equation under consideration. The best form of equation is then that for which the average of the squares of the deviations $(\Sigma D^2)/n$ is the least.

Differential Rate Data. Where accurate methods of chemical analysis are available, rate equations are best established from direct differential rate measurements in a differential reactor containing a bed of catalyst so small that relatively small changes of composition are obtained. Such apparatus should be designed to produce the smallest composition changes that permit accurate evaluation of the rate of reaction with the available analytical methods. Because of the exponential influence of temperature, it is desirable that the differential bed be at as uniform temperature as possible, requiring a small-diameter reactor with good heat-transfer provisions in the walls of the container.

In a differential reactor the average activity of each component may be taken as the arithmetic average of the inlet and outlet values for small changes or, better, derived from the logarithmic mean of the differences between the activities at the inlet and the outlet for the reactants. The mean activity of a product R may be taken as a_{Re} minus the log mean value of $(a_{Re} - a_R)$ at the terminal conditions where a_{Re} is the activity of R when the reaction proceeds to equilibrium. This use of log mean activities is merely an improved approximation which in general is not satisfactory except where concentration changes are small.

The adsorption-equilibrium constants which appear in the rate equations theoretically might be independently determined by adsorption measurements on the individual components. Such measurements may prove to be a valuable adjunct to direct catalytic rate measurements but are open to question because of the interaction effects and variability of active centers previously mentioned. Until these relations are better understood, these constants in the rate equations are best determined in the specific reaction under study by making rate measurements over a wide range of concentrations.

To minimize tedious algebraic solutions of simultaneous equations, it is desirable in complex systems to determine the effective average value of the absorption-equilibrium constant of each component by a constant-temperature series of at least three differential rate measurements in which the activity of that component is varied over a wide range while the activities of all other components are held constant. A convenient procedure is to make an initial run with the activity of each component at approximately the middle of the range of interest. Additional series of two runs each are then made in which the activity of each component is varied from a minimum value in one to a maximum in the other while the activities of all other components are held constant. This procedure may require two or more trials at some of the conditions with interpolation in order to obtain satisfactory constancy of the grouped activities but is not difficult with a flexible differential-reactor apparatus which permits wide variation in feed rates and depths of catalyst bed.

Once the adsorption-equilibrium constants are all evaluated, each single rate measurement permits calculation of the over-all rate constant C. These methods are demonstrated in the following illustration.

Illustration 2. Mixed iso-octenes, commercially known as codimer, are hydrogenated in the vapor phase to the corresponding iso-octanes according to the following reaction:

$$C_8H_{16}(g) + H_2(g) \rightleftarrows C_8H_{18}(g)$$

The reaction as it takes place on a supported nickel catalyst was studied in a pilot plant which was operated with a small bed of catalyst to approximate differential conditions. The experimental data are tabulated in Table A. These data were obtained when the catalyst was used at sufficiently high mass velocity that diffusional gradients were shown to be negligible, and the activities at the surfaces of the catalyst pellets may be assumed equal to those in the fluid stream. From these data it is desired to determine the probable mechanism of the reaction and to evaluate the constants of the corresponding rate equations. These experimental data and their interpretation are taken from the work of Tschernitz, Bornstein, Beckmann, and Hougen.[13]

The experimental procedure was planned to establish the effect of the average partial pressures of each component while holding the average partial pressures of the other two components nearly constant. However, the exact attainment of such conditions is not practical, since this would predicate advance knowledge of the exact effect of all the variables controlling the reaction rates.

In the operation of the experimental plant the rate of liquid flow was measured from

TABLE A

Experimental Data

Temperature = 200°C

		average values			r
Run	π	p_H	p_U	p_S	lb-mole/(lb)(hr)
1d	1.09	0.482	0.100	0.508	0.00353
3c	3.50	2.459	0.527	0.515	0.0250
3d	3.49	2.450	0.530	0.515	0.0320
10a	3.51	0.477	0.494	2.538	0.00553
11a	1.51	0.514	0.540	0.455	0.00870
11d	1.50	0.473	0.552	0.473	0.01392
11e	1.50	0.470	0.558	0.473	0.00960
12ab	1.105	0.104	0.562	0.440	0.00514
14a	3.52	0.450	2.840	0.230	0.01920
14b	3.51	0.409	2.810	0.289	0.0206
25a	2.50	0.484	1.075	0.942	0.0131
28b	2.10	0.357	1.590	0.153	0.0186

Temperature = 275°C

		average values			r
Run	π	p_H	p_U	p_S	lb-mole/(lb)(hr)
2a	1.105	0.478	0.102	0.525	0.00298
4d	3.520	2.505	0.518	0.497	0.0389
4e	3.500	2.500	0.517	0.485	0.0450
5b	3.510	0.425	2.770	0.310	0.0206
5d	3.500	0.433	2.800	0.270	0.0185
6bc	1.104	0.489	0.562	0.051	0.0180
7b	1.500	0.546	0.506	0.446	0.0103
7cd	1.500	0.469	0.556	0.475	0.01215
8bc	1.109	0.100	0.540	0.464	0.00705
9a	3.500	0.422	0.462	2.615	0.00824
9b	3.510	0.467	0.485	2.555	0.00734
26ab	2.500	1.495	0.511	0.495	0.0319
29ab	2.100	1.222	0.776	0.103	0.0435

[13] J. Tschernitz, S. Bornstein, R. B. Beckmann, and O. A. Hougen, *Trans. Am. Inst. Chem. Engrs.*, **42**, 883–903 (1946).

Temperature = 325°C

Run	π	average values			lb-mole/ (lb)(hr)
		p_H	p_U	p_S	
15a	3.50	0.500	2.735	0.270	0.0201
16a	1.10	0.482	0.560	0.062	0.0114
17b	1.50	0.501	0.533	0.466	0.0134
17c	1.50	0.475	0.553	0.471	0.00946
17e	1.50	0.476	0.556	0.478	0.00871
18a	1.10	0.101	0.548	0.451	0.0025
19b	3.50	2.335	0.550	0.610	0.0338
19c	3.50	2.540	0.452	0.510	0.0286
19d	3.50	2.405	0.524	0.572	0.0297
20ab	1.10	0.489	0.098	0.513	0.0044
21a	3.51	0.480	0.480	2.550	0.01106
24a	2.50	0.555	0.299	1.645	0.00533
27a	2.50	0.599	0.996	0.907	0.01885
30a	2.10	0.438	1.523	0.136	0.01414
30b	2.10	0.478	1.480	0.144	0.0159

the volume and density of the outgoing liquid, the outgoing hydrogen by a displacement meter, and the degree of conversion from the index of refraction of the ingoing and outgoing liquids. The composition of the liquid was related to the refractive index by previous calibration of known samples analyzed for unsaturates primarily by hydrogen absorption and secondarily by standard chemical analysis by the bromine method. The following ranges of variables were investigated: pressures from 1.0 to 3.5 atm, temperatures from 200 to 325°C, and feed compositions from 10 to 90 mole per cent of each component. The five different feed stocks used were previously purified by steam distillation to separate polymers and by passing through a bed of nickel catalyst in the absence of hydrogen to remove sulfur. Temperatures above 350°C could not be investigated because of catalyst disintegration. The calculations involved in a specific run are illustrated herewith.

Blank tests were made in the pilot plant in the absence of the catalyst to determine the extent of the uncatalyzed reaction. This was not detectable at 200°C and 275°C. At 325°C a slight reaction took place amounting to 1 to 5 per cent of the catalyzed reaction depending upon feed composition. This correction was made to establish the rate of the catalytic reaction at 325°C.

Run 3c:

Feed stock II, 54.1 mole per cent unsaturates
Average molecular weight 112.9
Temperature: Entering 195°, leaving 206°, average 200.5°C
Catalyst, 0.0440 lb; density = 86.4 lb per cu ft; volume = 0.000509 cu ft
Pressure, 3.500 atm
Liquid flow leaving reactor, 1206 milliliters per hr; specific gravity 0.710
Index of refraction at 25.00°C of liquid entering 1.40580
Index of refraction at 25.00°C of liquid leaving 1.40453
Difference 0.00127

Factor for conversion to percentage change = 5150
Percentage change in composition of unsaturate = (5150)(0.00127) = 6.54

$$\text{Liquid leaving} = \frac{(1206)(0.710)}{(112.9)(454)} = 0.01671 \text{ lb-mole per hr}$$

$$\text{Conversion} = (0.01)(0.01671)(6.54) = 0.001093 \text{ lb-mole per hr}$$

$$r = \frac{0.001093}{0.0440} = 0.02484 \text{ lb-mole}/(\text{hr})(\text{lb catalyst})$$

$$\text{Hydrogen leaving} = 14.02 \text{ cu ft per hr (standard conditions)}$$

$$= \frac{14.02}{359} = 0.03905 \text{ lb-mole per hr}$$

MATERIAL BALANCE

		lb-moles per hr	*Mole Per Cent*	*Partial Pressures*, atm
Entering				
Unsaturates	= (0.541)(0.01671) =	0.00904	15.90	0.557
Saturates	= (0.459)(0.01671) =	0.00767	13.49	0.472
Hydrogen	= 0.03905 + 0.00109 =	0.04014	70.61	2.471
Total		0.05685	100.0	3.500
Leaving				
Unsaturates	= 0.00904 − 0.00109 =	0.00795	14.26	0.499
Saturates	= 0.00767 + 0.00109 =	0.00876	15.71	0.550
Hydrogen	=	0.03905	70.03	2.451
Total		0.05576	100.0	3.500

Since the change in composition is small, the arithmetic average partial pressures may be taken. Thus,

$$\begin{aligned} p_U &= 0.528 \\ p_S &= 0.511 \\ p_H &= \underline{2.461} \\ \pi &= 3.500 \end{aligned}$$

Cross-sectional area of bed (1.05 in. diameter) = 0.00601 sq ft

Entering flow rate = 0.00904(112) + 0.00767(114) + 0.0401(2) = 1.967 lb per hr

$$G = \text{mass velocity} = \frac{1.967}{0.00601} = 328 \text{ lb}/(\text{hr})(\text{sq ft})$$

At this mass velocity and reaction rate r, the transverse partial-pressure gradients due to mass transfer are negligible.

$$\text{Gaseous space velocity of entering feed} = \frac{(0.05685)(359)}{0.000509} = 40{,}100 \text{ cu ft (at 0°C, 1 atm)}/(\text{cu ft})(\text{hr})$$

Over-All Equilibrium Constant. Before the mechanism of this reaction was studied, thermodynamic calculations were made to determine the reversibility of the reaction within the experimental range of pressures and temperatures. The equilibrium degrees of conversion in the hydrogenation of codimer are plotted against temperature for various total pressures in Fig. 188. These data were calculated from the standard free-energy equation based upon the hydrogenation of 2,4,4-trimethyl pentene-1:

$$\Delta G_T^\circ = -RT \ln K = -25{,}289 + 11.21T \log_{10} T - 0.001267T^2 + (0.0465)\,10^{-6}T^3 - 4.599T \quad \text{(a)}$$

This equation was established from standard absolute entropy values supplied by Parks.[14] The standard heat of formation of the paraffin was measured by Rossini,[15] and heat capacity of the paraffin was taken from the data of Pitzer and Scott.[16] The heat of formation and heat capacity of the olefin were estimated from Tables XXXIX–XLIII.

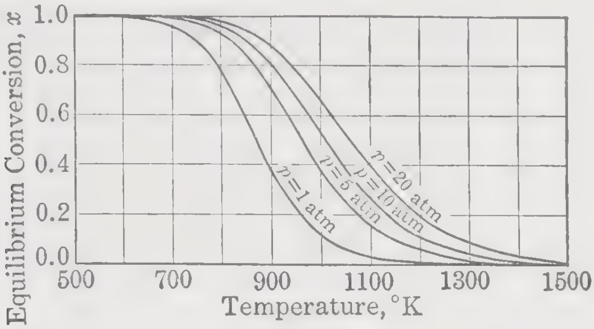

FIG. 188. Equilibrium Conversion of Codimer to Hydrogenated Codimer.

It may be observed from Fig. 188 that up to 650°K the reverse reaction is negligible. It was also found experimentally by Beckmann[17] that no decomposition occurred when vapors of iso-octane were passed through the catalyst at 300°C. Within the range of these experimental studies the effect of the reverse reaction can be neglected.

Determination of Mechanism of Reaction. Determination of the most plausible mechanism in the hydrogenation of codimer is based upon the assumptions that only one chemical step is rate-controlling. Upon this assumption 17 different mechanisms seem possible for the catalytic hydrogenation of codimer in the vapor phase. Diffusion of the gaseous components occurs independently and simultaneously with the chemical steps, but under the selected experimental conditions these steps offered negligible resistance. The possible chemical steps, together with their corresponding rate equations, expressed in convenient forms for comparison, are listed in the following pages. In comparing these equations with those presented previously (pages 911–926) it should be noted that the terms involving the reverse reaction drop out because of the high equilibrium constant. The subscript H refers to hydrogen, U to the unsaturated component, and S to the saturated component.

TABLE B

POSTULATED MECHANISMS

I. Reaction between molecularly adsorbed hydrogen and adsorbed codimer:

(*a*) Adsorption of hydrogen controlling:

$$R = \frac{p_H}{r} = \frac{1}{\alpha}(1 + K_U p_U + K_S p_S) = a + b p_U + c p_S$$

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[14] G. S. Parks, Private correspondence.

[15] F. D. Rossini, *Chem. Rev.*, **27**, 1–16 (1940).

[16] K. S. Pitzer and D. Scott, *J. Am. Chem. Soc.*, **63**, 2419 (1941).

[17] R. B. Beckmann, Ph.D. thesis, University of Wisconsin (1944).

(*b*) Adsorption of codimer controlling:

$$R = \frac{p_U}{r} = \frac{1}{\alpha}(1 + K_H p_H + K_S p_S) = a + f p_H + c p_S$$

(*c*) Desorption of hydrogenated codimer controlling:

$$R = \frac{p_H p_U}{r} = \frac{1}{\alpha K_H K_U}(1 + K_H p_H + K_U p_U) = a + f p_H + b p_U$$

(*d*) Surface reaction controlling:

$$R = \sqrt{\frac{p_H p_U}{r}} = \sqrt{\frac{1}{\alpha K_H K_U}}(1 + K_H p_H + K_U p_U + K_S p_S) = a + f p_H + b p_U + c p_S$$

II. Reaction between atomically adsorbed hydrogen and adsorbed codimer:

(*e*) Adsorption of hydrogen controlling:

$$R = \sqrt{\frac{p_H}{r}} = \sqrt{\frac{1}{\alpha}}(1 + K_U p_U + K_S p_S) = a + b p_U + c p_S$$

(*f*) Adsorption of codimer controlling:

$$R = \frac{p_U}{r} = \frac{1}{\alpha}(1 + \sqrt{K_H p_H} + K_S p_S) = a + f\sqrt{p_H} + c p_S$$

(*g*) Desorption of hydrogenated codimer controlling:

$$R = \frac{p_H p_U}{r} = \frac{1}{\alpha K_H K_U}(1 + \sqrt{K_H p_H} + K_U p_U) = a + f\sqrt{p_H} + b p_U$$

(*h*) Surface reaction controlling:

$$R = \sqrt[3]{\frac{p_H p_U}{r}} = \sqrt[3]{\frac{1}{\alpha K_U K_H}}(1 + \sqrt{K_H p_H} + K_U p_U + K_S p_S)$$
$$= a + f\sqrt{p_H} + b p_U + c p_S$$

III. Reaction between codimer in the gas phase and molecularly adsorbed hydrogen:

(*i*) Adsorption of hydrogen controlling:

$$R = \frac{p_H}{r} = \frac{1}{\alpha}(1 + K_S p_S) = a + c p_S$$

(*j*) Desorption of hydrogenated codimer controlling:

$$R = \frac{p_H p_U}{r} = \frac{1}{\alpha K_H}(1 + K_H p_H) = a + f p_H$$

(*k*) Surface reaction controlling:

$$R = \frac{p_H p_U}{r} = \frac{1}{\alpha K_H}(1 + K_H p_H + K_S p_S) = a + f p_H + c p_S$$

IV. Reaction of codimer in the gas phase and atomically adsorbed hydrogen:

(*l*) Adsorption of hydrogen controlling:

$$R = \sqrt{\frac{p_H}{r}} = \sqrt{\frac{1}{\alpha}}\,(1 + K_S p_S) = a + cp_S$$

(*m*) Desorption of hydrogenated codimer controlling:

$$R = \frac{p_H p_U}{r} = \frac{1}{\alpha K_H}\,(1 + \sqrt{K_H p_H}) = a + f\sqrt{p_H}$$

(*n*) Surface reaction controlling:

$$R = \sqrt{\frac{p_H p_U}{r}} = \sqrt{\frac{1}{\alpha K_H}}\,(1 + \sqrt{K_H p_H} + K_S p_S) = a + f\sqrt{p_H} + cp_S$$

V. Reaction between hydrogen in the gas phase and adsorbed codimer:

(*o*) Impact of hydrogen upon adsorbed codimer controlling:

$$R = \frac{p_H p_U}{r} = \frac{1}{\alpha K_H}\,(1 + K_U p_U + K_S p_S) = a + bp_U + cp_S$$

(*p*) Desorption of hydrogenated codimer controlling:

$$R = \frac{p_H p_U}{r} = \frac{1}{\alpha K_U}\,(1 + K_U p_U) = a + bp_U$$

(*q*) Adsorption of codimer controlling:

$$R = \frac{p_U}{r} = \frac{1}{\alpha}\,(1 + K_S p_S) = a + cp_S$$

VI. Uncatalyzed reaction in the gas phase:

(*r*)

$$R = \frac{r}{p_H p_U} = a$$

Interpretation of Data. The constants of the equations for the various proposed mechanisms were evaluated by the method of least squares. The four constants, *a*, *b*, *c*, and *f* were evaluated for each mechanism. It is a requirement of the theory upon which these equations are based that all constants must have positive or zero values. As an illustration, the method of evaluating the constants for mechanism *d* are given for the 12 runs made at 200°C.

The four simultaneous equations for evaluating the four constants by the method of least squares are as follows, where $R = \sqrt{\dfrac{p_H p_U}{r}}$ and $n = 12$.

$$an + b\Sigma p_U + c\Sigma p_S + f\Sigma p_H = \Sigma R \tag{b}$$

$$a\Sigma p_H + b\Sigma p_H p_U + c\Sigma p_H p_S + f\Sigma p_H^2 = \Sigma p_H R \tag{c}$$

$$a\Sigma p_U + b\Sigma p_U^2 + c\Sigma p_U p_S + f\Sigma p_U p_H = \Sigma p_U R \tag{d}$$

$$a\Sigma p_S + b\Sigma p_S p_U + c\Sigma p_S^2 + f\Sigma p_S p_H = \Sigma p_S R \tag{e}$$

TABLE C

EXPERIMENTAL DATA AND EVALUATION OF TERMS OF DETERMINANTS (MECHANISM *d*)

200°C

Run	p_U	p_S	p_U	r (lb-mole)/(lb) (hr)	$\frac{p_H p_U}{r}$	R	p_U^2	p_S^2	p_H^2	$p_H p_U$
1d	0.100	0.508	0.482	0.00353	13.6	3.68	0.0110	0.2581	0.2323	0.0482
3c	0.527	0.515	2.459	0.0250	51.9	7.18	0.2778	0.2652	6.0467	1.2959
3d	0.530	0.515	2.450	0.0320	40.6	6.35	0.2809	0.2652	6.0025	1.2985
10a	0.494	2.538	0.477	0.00553	42.5	6.50	0.2440	6.4414	0.2275	0.2356
11a	0.540	0.455	0.514	0.0087	31.9	5.65	0.2916	0.2074	0.2642	0.2776
11d	0.552	0.473	0.473	0.01392	18.7	4.32	0 3047	0.2237	0.2237	0.2611
11e	0.558	0.473	0.470	0.0096	27.1	5.20	0 3114	0.2237	0.2209	0.2623
12ab	0.562	0.440	0.104	0.00514	11.4	3.38	0.3158	0.1936	0.0108	0.0584
14a	2.840	0.230	0.450	0.0192	66.5	8.14	8.0656	0.0529	0.2025	1.2780
14b	2.810	0.289	0.409	0.0206	55.8	7.46	7.8961	0.0835	0.1673	1.1493
25a	1.075	0.942	0.484	0.0131	39.6	6.30	1.1556	0.8874	0.2343	0.5203
28b	1.590	0.153	0.357	0.0186	30.6	5.50	2.5281	0.0234	0.1274	0.5676
$\Sigma =$	12.178	7.531	9.129		430.2	69.66	21.681	9.125	13.960	7.253

TABLE C.—(*Continued*)

Run	p_Hp_S	p_Up_S	Rp_U	Rp_S	Rp_H	*R*, *Calc*	*R*, *Exp*	δ_R	δ_R^2	*Per Cent* δ_R
1d	0.2449	0.0508	0.368	1.869	1.774	3.97	3.68	0.29	0.084	7.88
3c	1.2664	0.2714	3.784	3.698	17.656	6.86	7.18	−0.32	0.102	−4.46
3d	1.2618	0.2730	3.366	3.270	15.557	6.86	6.35	0.51	0.260	8.03
10a	1.2106	1.2538	3.211	16.497	3.101	6.62	6.50	0.12	0.014	1.85
11a	0.2339	0.2457	3.051	2.571	2.904	4.63	5.65	−1.02	1.04	−18.05
11d	0.2237	0.2611	2.385	2.043	2.043	4.62	4.32	0.30	0.09	6.94
11e	0.2223	0.2639	2.902	2.460	2.444	4.62	5.20	−0.58	0.336	−11.15
12ab	0.0458	0.2473	1.900	1.487	0.352	4.18	3.38	0.80	0.640	23.66
14a	0.1036	0.6532	23.118	1.872	3.663	7.84	8.14	−0.30	0.090	−3.69
14b	0.1182	0.8121	20.963	2.156	3.051	7.81	7.46	0.35	0.123	4.69
25a	0.4559	0.0127	6.773	5.935	3.049	5.40	6.30	−0.40	0.160	−6.35
28b	0.0546	0.2433	8.745	0.842	1.964	5.75	5.50	0.25	0.063	4.54
Σ =	5.442	5.588	80.566	44.700	57.558				$\Sigma = 3.002$	±8.44 (average)

The indicated summations are summarized in Table C. Introduction of these values gives

$$12.000a + 12.178b + 7.531c + 9.129f = 69.660 \quad (f)$$

$$9.129a + 7.253b + 5.442c + 13.960f = 57.558 \quad (g)$$

$$12.178a + 21.682b + 5.588c + 7.253f = 80.566 \quad (h)$$

$$7.531a + 5.588b + 9.125c + 5.442f = 44.700 \quad (i)$$

By the elimination of a three equations result for further evaluation by determinants.

$$0.2203b + 0.0315c - 0.7685f = -0.5001 \quad (j)$$

$$-0.9860b + 0.1372c + 0.9336f = -0.3112 \quad (k)$$

$$1.0385b - 0.7527c - 0.1269f = 0.6808 \quad (l)$$

Solving the last three equations by determinants gives

$$b = 1.526$$

$$c = 1.010$$

$$f = 1.129$$

By substitution in any of the foregoing four-term equations, $a = 2.764$.

Similar calculations were made for all 17 mechanisms and for all experimental data at the other two temperature levels. The resultant values of a, b, c, and f are summarized in Tables D, E, and F. From inspection of Table D for runs at 200°C it may be observed that all mechanisms except d and h may be rejected, because certain constants are negative or are not zero when demanded. For example, mechanism r, corresponding to the uncatalyzed reaction, is unsatisfactory for four reasons, since a is negative, and b, c, and f are not zero. Rejection of this mechanism would be expected from the very function of the catalyst. The acceptable mechanism d corresponds to the reaction between activatedly adsorbed molecular hydrogen and codimer to give the activatedly adsorbed product; mechanism h is similar except that atomic hydrogen is involved. The experimental fit is better with mechanism d. Mechanism d seems more logical than h, since no dissociation of molecular hydrogen is required by the hydrogenation reaction. The acceptable equation for the rate of hydrogenation at 200°C is therefore

$$R = \sqrt{\frac{p_H p_U}{r}} = 2.764 + 1.526p_U + 1.010p_S + 1.129p_H \quad (m)$$

The accuracy of this equation for any particular experimental run is established by comparing calculated with experimental values by the standard deviation squared, δ^2, where δ is the difference between calculated and experimental values of R. The percentage deviation of individual runs is given as $100\delta/R$ where R is the experimental value. These values are recorded in the last three columns of Table C. It may be observed that the average percentage deviation for individual runs is ±8.4 per cent; the experimental accuracy of individual runs is no better than this because of the small changes in composition obtained in the small catalyst beds. Runs 11a and 12ab show large deviations. Greater degrees of conversion can be obtained by using larger beds, but this introduces even greater errors due to uncertainties in average values of temperatures and partial pressures.

Evaluation of Constants in the Rate Equations. The experimental values of a, b, c, and f for the accepted mechanism d are recorded in Table G for the three temperature levels and plotted in Fig. 188a on log constant–reciprocal temperature co-ordinates.

Since the several constants a, b, c, and f are each products and quotients of adsorption-equilibrium constants and one reaction velocity constant as shown in Equation (d) of Table B, they would be expected to plot as nearly straight lines on log constant–reciprocal temperature plots. In this respect it may be observed that the values of a and b plot well, f plots fairly well, but c plots poorly. The best straight lines on this logarithmic reciprocal plot were established by the method of least squares for each constant. The corrected values obtained from the straight lines are recorded in Table G for the three temperature levels.

TABLE D

CONSTANTS FOR VARIOUS MECHANISMS AT 200°C

Mechanism	a	b	c	f	*Reasons for Rejection*	
a	54.6	−19.4	12.1	16.3	f should be 0	b should be +
b	44.0	36.4	14.8	−22.6	b should be 0	f should be +
c	−101	44.0	117	24.3	c should be 0	a should be +
d	2.76	1.53	1.01	1.13	Acceptable	
e	5.64	−1.31	0.89	2.73	f should be 0	b should be +
f	66.9	36.5	15.5	−51.8	b should be 0	f should be +
g	−115	42.4	114	45.0	c should be 0	a should be +
h	0.736	0.781	1.29	1.09	Acceptable	
i	54.6	−19.4	12.1	16.3	b should be 0 f should be 0	
j	−101	44.0	117	24.3	b should be 0 c should be 0	a should be +
k	−101	44.0	117	24.3	b should be 0	a should be +
l	5.64	−1.31	0.89	2.73	b should be 0 f should be 0	
m	−115	42.4	114	45.0	b should be 0 c should be 0	
n	1.74	1.50	0.95	2.46	b should be 0	
o	−101	44.0	117	24.3	f should be 0	a should be +
p	−101	44.0	117	24.3	c should be 0 f should be 0	a should be +
q	44.0	36.4	14.8	−22.6	b should be 0 f should be 0	
r	−101	44.0	117	24.3	b should be 0 c should be 0 f should be 0	a should be +

From the corrected constants a, b, c, and f the equilibrium-adsorption constants K_H, K_U, and K_S and the over-all surface-reaction rate constant $\alpha = Ek$ were obtained from the following relations:

$$K_U = \frac{b}{a}; \quad K_S = \frac{c}{a}; \quad K_H = \frac{f}{a} \quad \text{and} \quad \alpha = \frac{1}{a^2 K_H K_U} \tag{n}$$

These fundamental constants are recorded in Table G for the three temperatures.

The adsorption-equilibrium constants can be expressed in terms of temperature by the following general relationship:

$$\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{o}$$

Provided the catalyst activity remains unaltered with change in temperature the constants ΔH and ΔS correspond to the effective enthalpy and entropy changes, respectively, in activated adsorption; otherwise they are empirical only.

TABLE E

CONSTANTS FOR VARIOUS MECHANISMS AT 275°C

Mechanism	*a*	*b*	*c*	*f*	*Reasons for Rejection*	
a	63.0	−19.0	2.87	1.0	*f* should be 0	*b* should be +
b	31.3	41.8	8.01	−21.0	*b* should be 0	*f* should be +
c	3.98	18.9	4.45	5.97	*c* should be 0	
d	2.84	1.60	0.494	0.687	Acceptable	
e	7.12	−1.61	0.370	0.810	*f* should be 0	*b* should be +
f	13.0	67.4	15.4	−31.7	*b* should be 0	*f* should be +
g	−311	22.2	7.65	40.8	*c* should be 0	*a* should be +
h	1.74	0.606	0.216	0.644	Acceptable	
i	63.0	−19.0	2.87	1.0	*b* should be 0 *f* should be 0	
j	3.98	18.9	4.45	5.97	*b* should be 0 *c* should be 0	
k	3.98	18.9	4.45	5.97	*b* should be 0	
l	7.12	−1.61	0.370	0.810	*b* should be 0 *f* should be 0	
m	−311	22.2	7.65	40.8	*b* should be 0 *c* should be 0	
n	2.12	1.60	0.500	1.53	*b* should be 0	
o	3.98	18.9	4.45	5.97	*f* should be 0	
p	3.98	18.9	4.45	5.97	*c* should be 0 *f* should be 0	
q	31.3	41.8	8.01	−21.0	*b* should be 0 *f* should be 0	
r	3.98	18.9	4.95	5.97	*b* should be 0 *c* should be 0 *f* should be 0	

The term effective is used here to distinguish the values of ΔH and ΔS effective in catalysis from those values obtained by separate adsorption of the pure component gases in the absence of a catalytic reaction. The values of ΔH and ΔS for each component are recorded in Table G.

The rate constant α is made up of the surface-reaction velocity constant k and the effectiveness factor E where $\alpha = Ek$. The constant α can be written in the usual Arrhenius form, thus

$$\ln \alpha = -\frac{A}{RT} + \frac{B}{R} \tag{p}$$

In this investigation A was found to be $+1740$, and B was found to be 2.82.

If the effectiveness factor were assumed to be unity, then according to the Eyring theory (page 808), A could be taken as the enthalpy of activation in forming the activated complex, $\Delta H^{\ddagger} = 1740$, and B could be taken as the entropy of activation, $\Delta S^{\ddagger} = 2.82$. The low value of $\Delta H^{\ddagger}$ and the positive value of $\Delta S^{\ddagger}$ are both consistent with the properties of an effective catalyst such as the one under investigation. It should be noted that if the catalyst activity does not remain constant with temperature change the adsorption values of ΔH and ΔS for different gases become empirical constants and do not correspond to the true enthalpies and entropies of adsorption.

TABLE F

CONSTANTS FOR VARIOUS MECHANISMS AT 325°C

Mechanism	*a*	*b*	*c*	*f*	*Reasons for Rejection*	
a	63.0	−23.3	2.35	11.7	*f* should be 0	*b* should be +
b	54.0	33.8	−8.35	−10.7	*b* should be 0	*c* should be +
c	9.97	20.1	0.623	8.11	*c* should be 0	*f* should be +
d	3.75	1.60	0.039	0.697	Acceptable	
e	7.01	−1.64	0.108	1.77	*f* should be 0	*b* should be +
f	124	26.7	−11.4	−84.1	*b* should be 0	*c* should be +
g	2.29	20.2	0.376	17.3	*c* should be 0	*f* should be +
h	2.17	0.593	0.010	0.598	Acceptable	
i	63.0	−23.3	2.35	11.7	*b* should be 0 *f* should be 0	
j	9.96	20.1	0.623	8.11	*b* should be 0 *c* should be 0	
k	9.96	20.1	0.623	8.11	*b* should be 0	
l	7.01	−1.64	0.108	1.77	*b* should be 0 *f* should be 0	
m	2.29	20.2	0.376	17.3	*b* should be 0 *c* should be 0	
n	3.00	1.61	0.0114	1.60	*b* should be 0	
o	9.96	20.1	0.623	8.11	*f* should be 0	
p	9.96	20.1	0.623	8.11	*c* should be 0 *f* should be 0	
q	53.9	33.8	−8.35	−10.7	*b* should be 0 *f* should be 0	*c* should be +
r	9.96	20.1	0.623	8.11	*b* should be 0 *c* should be 0 *f* should be 0	

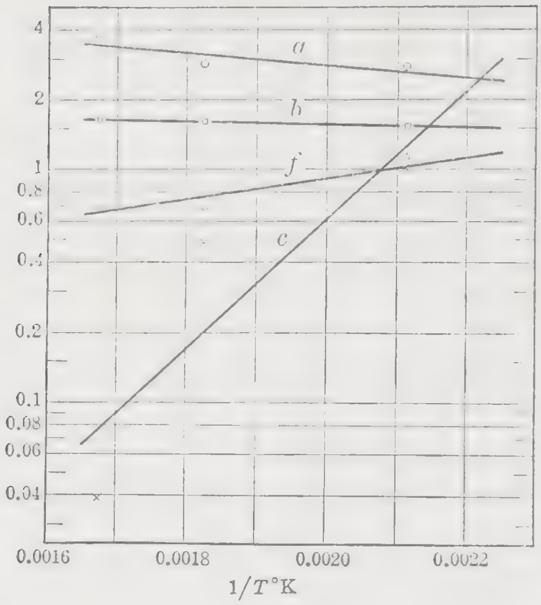

FIG. 188*a*. Experimental Values of Constants.

The final recommended equation for the vapor-phase hydrogenation of codimer by the given catalyst is as follows:

$$\left.\begin{aligned}
r &= \frac{EkK_{\mathrm{H}}K_{\mathrm{U}}\left[p_{\mathrm{H}}p_{\mathrm{U}} - \dfrac{p_{\mathrm{S}}}{K}\right]}{[1 + K_{\mathrm{H}}p_{\mathrm{H}} + K_{\mathrm{U}}p_{\mathrm{U}} + K_{\mathrm{S}}p_{\mathrm{S}}]^2}\\
\text{where}\qquad \ln K_{\mathrm{H}} &= +\frac{3110}{RT} - \frac{8.49}{R}\\
\ln K_{\mathrm{U}} &= +\frac{940}{RT} - \frac{3.08}{R}\\
\ln K_{\mathrm{S}} &= +\frac{13{,}700}{RT} - \frac{30.46}{R}\\
\ln Ek &= -\frac{1740}{RT} + \frac{2.82}{R}\\
&K \text{ is given by Equation (a).}
\end{aligned}\right\} \qquad \text{(q)}$$

From an inspection of Equation (q) and of Fig. 189 it may be observed that an increase in temperature has opposing effects on the reaction and adsorption constants. The surface-reaction velocity constant k increases with rise in temperature, whereas the adsorption-equilibrium constants decrease with rise in temperature. The net result of these conflicting effects is that the reaction rate increases with rise in temperature at a low-temperature range and decreases with rise in temperature at a higher-temperature range and yet at temperatures far below the region at which the reverse rate becomes appreciable. Above the optimum temperature the rate diminishes owing to desorption of reactant gases which more than offsets the accelerating

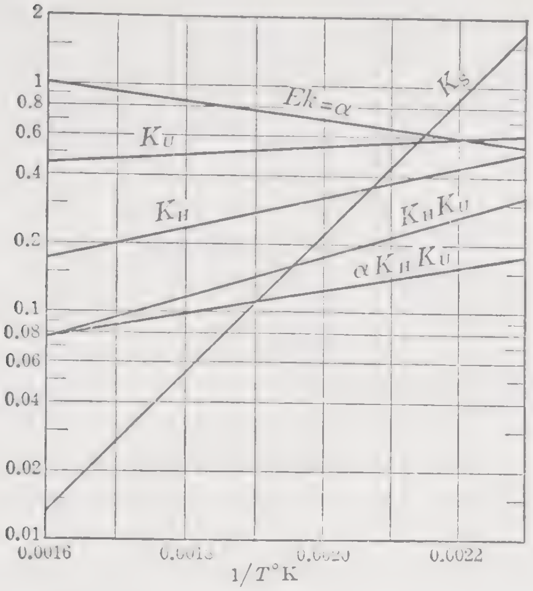

FIG. 189. Rate-Equation Constants for the Hydrogenation of Codimer.

TABLE G

SUMMARY OF THERMODYNAMIC CONSTANTS

	t 200°C	t 275°C	t 325°C
a (experimental)	2.764	2.84	3.753
b (experimental)	1.526	1.60	1.603
c (experimental)	1.010	0.494	0.0393
f (experimental)	1.129	0.687	0.697
a (corrected)	2.64	3.14	3.43
b (corrected)	1.53	1.58	1.61
c (corrected)	1.29	0.203	0.0762
f (corrected)	1.01	0.774	0.653
$\alpha = Ek$	0.644	0.830	0.954
K_U	0.580	0.503	0.469
K_S	0.489	0.0646	0.0222
K_H	0.383	0.246	0.190
$K_H K_U$	0.222	0.123	0.0891
$\alpha K_H K_U$	0.143	0.102	0.0850

$\Delta H_U = -940$

$\Delta H_S = -13{,}700$

$\Delta H_H = -3110$

$A = 1740$

$A + \Delta H_H + \Delta H_U = -2310$

$\Delta S_U = -3.08$

$\Delta S_S = -30.46$

$\Delta S_H = -8.49$

$B = 2.82$

$B + \Delta S_H + \Delta S_U = -8.76$

effect of temperature on the reaction among the molecules remaining adsorbed. This retardation of a reaction rate with increase in temperature is characteristic of many reactions which are catalyzed by solid surfaces. At low-temperature ranges an increase in temperature causes an increase in reaction rate owing to increased activation, whereas at high-temperature ranges the reaction is slow due to decreased adsorption of the reactants.

The general methods demonstrated in Illustration 2 are also applicable to moderately complex reacting systems in which several simultaneous and successive reactions may occur. It is only necessary that all products be clearly defined compounds which can be introduced into feed mixtures to simulate in the differential reactor conditions at various points of an integral reactor. The rates of the individual reactions are calculated from stoichiometric balances, and the rate equations are evaluated from the variation of these rates with varying activities of the components of the system.

Integral-Conversion Data. Wherever the precision of chemical analysis permits its use, the direct measurement of differential-reaction rates, as discussed in the preceding section, is the most satisfactory method for studying the kinetics of a not too complex system of catalytic reactions. However, there are many cases where the differential reactor is not satisfactory, due either to the inaccuracy of the available analytical methods or to the formation of complex products of side reactions which are not readily reproduced as components in the synthetic feed to a differential reactor. Under such circumstances it is necessary to work with integral-conversion data where large changes in composition are produced with low space velocities.

Differential rates can be obtained by plotting conversion x against W/F for a series of runs on a feed of given composition processed at constant temperature and pressure. If the diffusion of components to and from the catalyst particles is of importance, W/F is preferably varied by W being changed instead of F. From Equation (63) it is evident that the slope of such a curve is equal to r, the differential reaction rate. Thus a differential reaction rate may be determined either by a single run in a differential reactor or by a series of runs in an integral reactor. Once the differential rates are established, the method of analysis is the same as that discussed in the preceding section.

As pointed out in Chapter XVIII, pages 853–4, the evaluation of the constants in a differential-rate equation by graphically differentiating integral-conversion curves, although theoretically sound, is generally subject to large errors, depending on the procedure followed in drawing the curves and establishing the slopes. For this reason it is necessary to average a number of determinations corresponding to different conversions in order to obtain constants which satisfactorily represent the data. After such average values are determined, they are used to calculate an integral-conversion curve from Equation (64) for comparison with the experimentally determined conversions. This integration is readily carried out by plotting from the experimental data the activities of the various components of the system as functions of W/F. From these curves and the rate constants being tested reaction rates r are calculated, and a curve is plotted relating r as ordinates to W/F. The area under this curve between zero and any value of W/F gives the calculated conversion. The constants of the rate equation are adjusted by successive trials until satisfactory agreement is obtained between the experimental conversions and those calculated by integration. This method is tedious but may be applied to very complex systems.

The constants of a rate equation may be calculated by the direct application of an integral-conversion equation of the type shown in Table LVII if only a single reaction is involved or if the over-all results of more than one reaction may be treated as equivalent to a single reaction. The curves in Fig. 184 relate conversion to catalyst/feed ratio W/F, for the catalytic production of toluene from benzene plus xylene. For complete and direct evaluation of the rate equation such curves should be available at series of different temperatures, pressures, and feed compositions. However, where minimum data are available and the system is sufficiently simple to permit use of an integral-conversion equation it may be possible to evaluate the constants of the equation from merely three sets of curves such as Figs. 183, 184, and 185 in which pressure, space velocity, and temperature are independently varied. This procedure was followed by Johanson and Watson, who assumed that Equation (69) may be used to express the rate of production of toluene from an equimolal feed even though some toluene results from disproportionation of xylene as well as its reaction with benzene. This equation form was selected on the basis of the shape of the pressure relationship shown in Fig. 183. It may be noted that at low pressures the conversion is greatly increased by increase in pressure, whereas at high pressures further increase has little effect. Since thermodynamic data indicate that equilibrium is not approached at the high-pressure conditions, it was concluded that this form of variation is consistent with control of the reaction rate by a surface reaction involving dual active centers. The rate of such a reaction is proportional to the concentration of adjacently adsorbed xylene and benzene molecules and is expressed by Equation (69), including the fouling factor. At low pressures the denominator is substantially constant at 1.0, and the rate is proportional to the square of the pressure. At high pressures the denominator becomes proportional to the square of the pressure and the rate becomes independent of pressure.

The constants in Equation (69) were evaluated for a pure feed by use of the integrated form, Equation (e) of Table LVII. Consideration was first given to the data of Figs. 182 and 183 for short process periods where $\tau = 0$ and the fouling factor $B\pi$ is zero. As a first approximation it was assumed that because of the chemical and physical similarity of the reactants and products $K_R = (K_A + K_B)/2$. With this assumption β of Equation (e) becomes zero, leaving the following simplified equation:

$$\frac{C}{4}\left(\frac{W}{F}\right) = \frac{\alpha^2}{2\gamma} \ln \frac{(ax - 1 - \gamma)(-1 + \gamma)}{(ax - 1 + \gamma)(-1 - \gamma)} \tag{88}$$

Equation (88) contains only C and α as unknown constants if K is taken from the thermodynamic data of Pitzer and Scott.[18] These constants are evaluated by the calculation of values of $\alpha/\sqrt{C}$ at various pressures from the $\tau = 0$ curve of Fig. 183. The slope of the best straight line through a plot of $\alpha/\sqrt{C}$ against $1/\pi$ is equal to $1/\sqrt{C}$, and the intercept is equal to $(K_A + K_B)2/\sqrt{C}$ or $K_{AB}/\sqrt{C}$.

With these two constants evaluated the assumption that $K_R = K_{AB}$ was verified by using Equation (88) to calculate a curve relating W/F to x for comparison with the $\tau = 0$ curve of Fig. 184. The agreement was satisfactorily within the probable accuracy of the data. Had the calculated curve given conversions not in agreement with the data at high values of W/F it would have been necessary to evaluate a first approximation value of K_R by applying Equation (e) to experimental data in the high-conversion range and solving for β. A finite value of β would then require re-evaluation of K_{AB} and C and then calculation of a second approximation of K_R.

The effects of temperature on C and K_{AB} were determined from the $\tau = 0$ data of Fig. 185. These constants may be expressed as functions of temperature by the following equations involving the values already determined at 932°F (773°K):

$$C = C_{773}e^{-\frac{b_c}{R}\left(\frac{1}{T} - \frac{1}{773}\right)} \tag{89}$$

$$K_{AB} = (K_{AB})_{773}e^{\frac{-\Delta H_{AB}}{R}\left(\frac{1}{T} - \frac{1}{773}\right)} \tag{90}$$

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[18] K. S. Pitzer and D. W. Scott, *J. Am. Chem. Soc.*, **65**, 803 (1943).

By combining (88), (89), and (90) an equation is obtained which contains only two unknown constants, b_c and ΔH_{AB}. These are evaluated by applying the equation to a high-temperature and to a low-temperature point on the $\tau = 0$ curve of Fig. 185. The resulting two equations are simultaneously solved by assuming values of b_c and calculating the corresponding values of ΔH_{AB} from each equation. The intersection of the two curves relating ΔH_{AB} to b_c evaluates the constants.

The fouling factor terms of Equation (69) enter into both α and β of Equation (e), Table LVII. Values of $u\tau^b$ at 932°F are obtained by estimating the initial reaction rates where $x = 0$ by measuring the slopes of the curves of Fig. 184 at the origin. Where $x = 0$, Equation (69) reduces to the following:

$$r_0 = \frac{C}{4\left[\frac{1}{\pi} + K_{AB} + u\tau^b\right]^2} = \frac{C}{4\alpha^2} \tag{91}$$

The constants u and b are readily calculated from values of r_0 for different values of τ. Since an unguided graphical determination of slope at the origin is difficult, better results are obtained by calculating r_0 for $\tau = 0$ from the known constants C and K_{AB} and then assuming that the values of r_0 are proportional to the values of x read from the curves where $W/F = 10$. This same method is used for evaluating u at the lowest temperature of Fig. 185, it being assumed that at the low conversions involved the initial rates of reaction are proportional to conversion. It is assumed that b is independent of temperature and that u is related to temperature by an equation of the form of (89).

Values of v and c are obtained by solving Equation (e) of Table LVII for β at different values of τ at each of two temperatures where high conversions are obtained. In this manner all of the constants are evaluated as functions of temperature as summarized in Table LVIII.

This method of evaluating a rate equation has the advantage of permitting accurate determination of constants from a minimum of experimental data. However, the integrated-conversion equations are almost invariably of such complex form that the calculations are very tedious. A high order of numerical accuracy with 6 to 8 significant figures is necessary in most of this work, because the result is generally a small difference between two large logarithmic terms of opposite sign.

Empirical Conversion Plots. Simplified approximate correlations of kinetic data which have no sound theoretical bases are dangerous and must be used with constant consideration of the assumptions and possible errors involved, particularly in extrapolating away from the ranges

TABLE LVIII

Rate-Equation Constants

$K = e^{(682.3/RT)+(1.539/R)}$
(Temperature range of 700–1050° F)

$C = 7.56\, e^{\frac{-13{,}000}{RT}}$
(mole)/(mass of catalyst) (hr) $(\text{atm})^2$

$K_A = K_B = K_R = e^{(5{,}000/RT)-(9.54/R)}$
(1/atm)

$u = 131\, e^{\frac{-16{,}691}{RT}}$
$1/(\text{atm})\ (\text{min})^{0.63}$

$b = 0.63$

$v = 9820\, e^{\frac{-23{,}149}{RT}}$
1/(atm) (min)

$c = 1.0$

of experimental experience. However, in many cases such approximate empirical methods can be effectively used with great savings in time.

A most useful basis for correlating and predicting the effects of variations in space velocity is to assume that even complex catalytic systems approximate a pseudo-first-order relationship when only space velocity or feed rate is varied, keeping the temperature, pressure, and the proportions of reactants all constant. Consideration of the curves of Fig. 190 indicates that this assumption is at least qualitatively correct for this system. As the amount of catalyst is increased, the conversion increases toward equilibrium at a progressively diminishing rate, exactly as in a simple first-order reaction where the rate of reaction is proportional to the activity of the unconverted reactant. The conversion W/F curves of many catalytic reactions follow this general form at any one set of conditions, even though the effects of varying temperatures, pressures, and compositions are most complex.

Assumption of pseudo-first-order behavior leads to the following rate equation for a pure reactant A:

$$r_A = k\left(1 - x_A - \frac{x_A}{K}\right) = k\left(1 - \frac{x_A}{x_A^*}\right) \tag{92}$$

where r_A = rate of reaction of A, mole/(mass of catalyst) (unit time)
k = apparent-reaction velocity constant
x_A = mole fraction of A converted
K = equilibrium constant of reaction
x_A^* = mole fraction of A at equilibrium = $1/(1 + 1/K)$

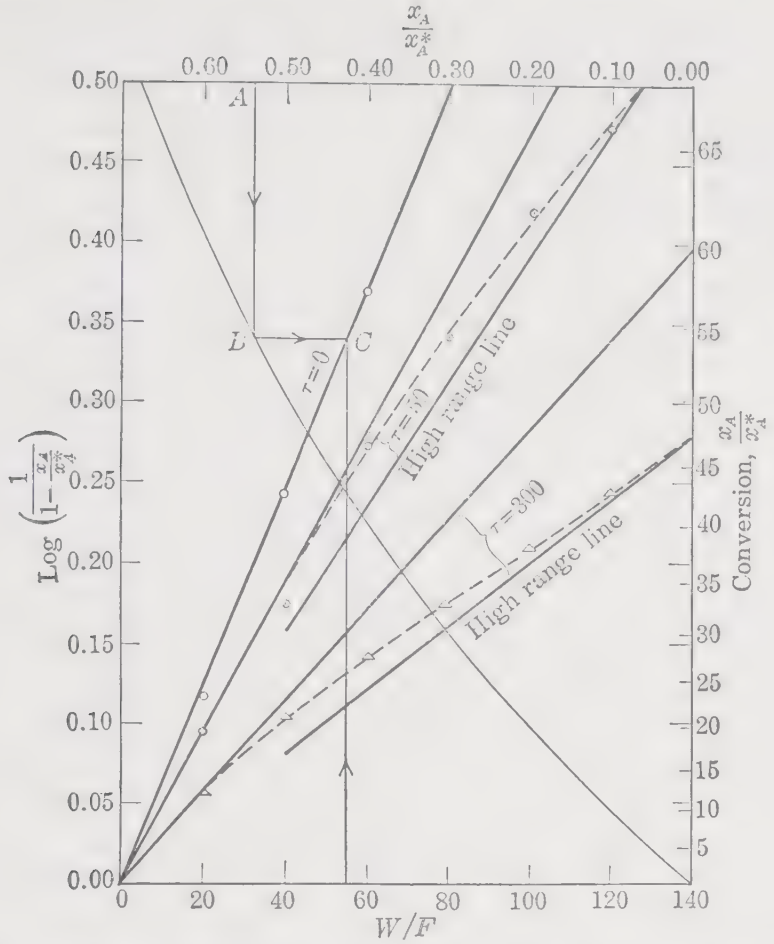

FIG. 190. Linear Co-ordinates for Pseudo-First-Order Kinetics (Low Conversion Range).

(Reproduced in "C.P.P. Charts")

Combining Equations (92) and (60) gives

$$\frac{W}{F} = \frac{1}{k}\int_0^{x_A} \frac{dx_A}{\left(1 - \frac{x_A}{x_A^*}\right)} = \frac{x_A}{k} \ln\left(\frac{1}{1 - \frac{x_A}{x_A^*}}\right) \tag{93}$$

It is evident from Equation (93) that where pseudo-first-order behavior is approximated linear relationships should result from plotting W/F or reciprocal space velocity against log $1/(1 - x_A/x_A^*)$, or F/W or space velocity against $\frac{1}{\log 1/(1 - x_A/x_A^*)}$. A convenient method of arranging such plots on rectangular-co-ordinate paper is shown in Figs. 190 and 191. In each plot a nonuniform ordinate scale for conversion x_A/x_A^* is established by means of the curve relating conversion on the upper scale of abscissas to conversion on the ordinate scale. As an example of the use of such a plot consider a conversion of 54 per cent with a value of W/F equal to 55, $[F/W = (1.82)10^{-2}]$. The point C is plotted by entering either chart at point A on the upper scale of abscissas, following down to the curved line at B, and then horizontally to the proper abscissa value

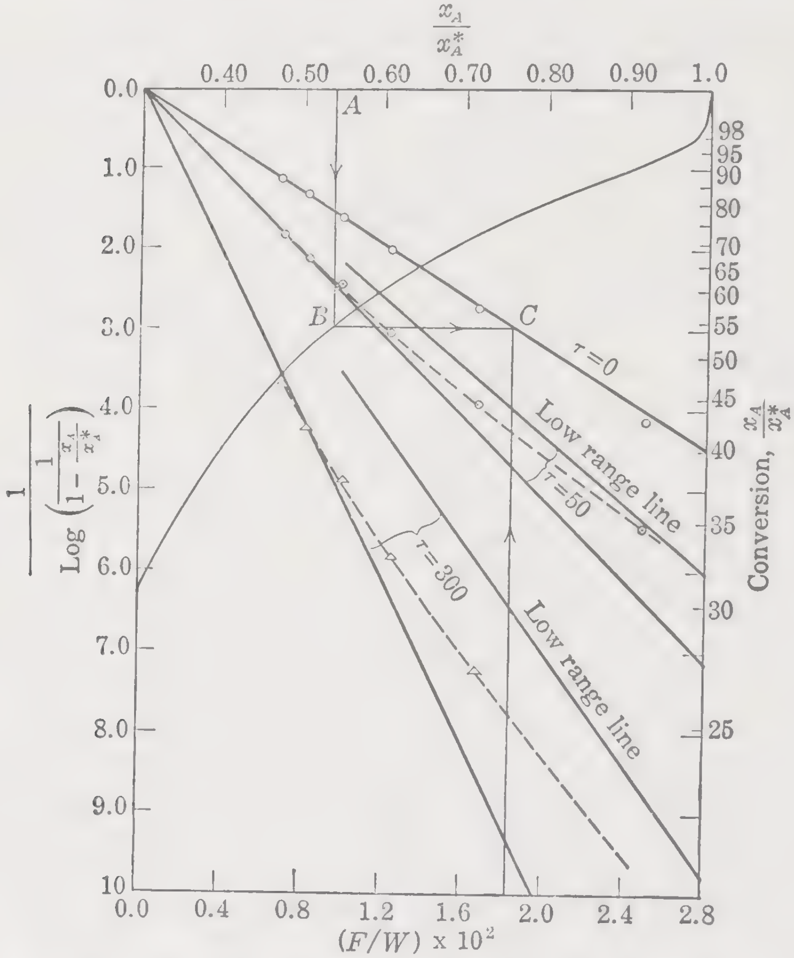

FIG. 191. Linear Co-ordinates for Pseudo-First-Order Kinetics (High Conversion Range).

(Reproduced in " C.P.P. Charts ")

at C. A truly first-order reaction plotted in this manner will yield straight lines, the slopes of which are proportional to the reaction velocity constant. Figure 191 is useful for the high-conversion low-space-velocity range, because all curves must extrapolate to $x_A/x_A^* = 1.0$ where the space velocity is zero. Figure 190 is useful for the low-conversion high-space-velocity range where all curves converge at zero conversion and zero W/F or reciprocal space velocity.

These charts may be used for empirically plotting either the ratios of conversion to equilibrium conversion or the ratio of yield of a product to its ultimate yield at 100 per cent conversion. If pseudo-first-order behavior is approximated, a single experimental point serves to establish an approximate relationship between space velocity and conversion over the entire range.

To test the applicability of this approximation, points from the curves of Fig. 184 are plotted on Figs. 190 and 191. The broken lines are average curves through the points, whereas the straight lines are drawn from the extreme points to the origin on each chart. It may be noted that the points from the curve for short process periods ($\tau = 0$) are in excellent agreement with the first-order approximation over the entire range. However, the points corresponding to process periods of 50 and 300 min show increasing deviation from the linear relationships, indicating that the effective first-order-reaction velocity constant diminishes progressively with increased conversion. In these cases considerable error would result from assumption of a linear relationship based on a single point. However, a fair approximation may be obtained from two results, one at high and one at low space velocity. The low-space-velocity point is used to establish a line on Fig. 191 and the high-space-velocity point to establish a line on Fig. 190. The high-range line is then plotted on the low-range chart and the reverse, and the two lines are joined by smooth curves similar to the broken-line curves of Figs. 190 and 191.

This method of plotting is useful for correcting experimental results to a common space-velocity basis for correlation and for making preliminary extrapolations of space-velocity relationships. It is also convenient for comparing different catalysts and estimating the different space velocities required for a given conversion. However, it must be emphasized that, even though such empirical methods may give excellent agreement with observed conversion–space-velocity relationships, this gives no basis for assuming that the effects of pressure, temperature, and composition variations bear any similar relationship to first-order behavior.

Complex Reactions. As previously mentioned the general methods developed for analysis of data for the relatively simple systems discussed in the preceding sections also may be applied to complex systems involving several simultaneous reactions. This situation is common for high-temperature catalytic reactions of organic compounds. In addition to several catalytic reactions there are frequently important uncatalyzed reactions which occur in the void spaces of the catalyst bed and in the preheating and cooling sections of the reactor. It is evident that reactions of such widely different mechanisms may be affected quite differently by changes in operating conditions, and the resulting relationships may be very complex. Under such conditions the inherent inaccuracy of catalytic data may make it difficult to establish firmly even the direction of trends of considerable commercial significance.

There are many advantages to be gained by resolving a complex reacting system into its component individual reactions and evaluating a quantitative expression for the rate of each. It may be necessary to resort to semiempirical methods such as are discussed in Chapter XVIII, but the resulting equations will be relatively simple in form. The individual reactions are best studied over wide ranges of conditions which are representative of those in the complex system. By combining individual rate equations properly evaluated in this manner it may be possible to predict by calculation the behavior of the complex system with greater accuracy than by direct experimental measurements over limited ranges.

The dehydrogenation of *n*-butane to form butenes over a chromia–alumina catalyst at temperatures of the order of 1100°F is an example of such a system. The principal reaction is the removal of 1 mole of hydrogen according to the following equation:

$$C_4H_{10} \rightleftarrows C_4H_8 + H_2$$

Secondary dehydrogenation of butene to butadiene also occurs.

$$C_4H_8 \rightleftarrows C_4H_6 + H_2$$

At the high temperatures used these reactions take place to an appreciable extent by pyrolysis in the homogeneous phase as well as by catalysis. In addition, the following reactions occur by both pyrolytic and catalytic mechanisms:

(*a*) The dealkylation or cracking of butane to form methane, ethane, ethylene, and propylene.

(*b*) The dealkylation of butenes to form methane, ethane, propane, ethylene, propylene, and carbon.

(*c*) The dimerization of butadiene to form 4-vinyl cyclohexene-1.

(*d*) The decomposition of butadiene to form hydrogen, methane, ethylene, acetylene, and carbon.

A complete kinetic analysis of this system should include measurements of the rates of all of these reactions, both catalyzed and uncatalyzed. The uncatalyzed reactions are evaluated by replacing the catalyst bed by a noncatalytic material such as fused quartz. The effects of catalytic reactions are then segregated by subtracting from the over-all results those which may be attributed to pyrolysis. In this manner, by working first with the reactions of the terminal products and then of the intermediate products, it is possible to evaluate by difference the results of reactions which cannot be isolated.

A preliminary study of the catalytic dehydrogenation of butane was carried out by Dodd and Watson[19] who developed a simplified analysis in which only three rate equations were used to represent the behavior of the system. The secondary formation of butadiene and its reactions were neglected, and it was assumed that the cracking of butane and butenes occurred by pseudo-first-order reactions having the same velocity constants. Product distributions were assigned to these reactions on the basis of data in the literature for uncatalyzed pyrolysis. Thus, the three reactions considered were:

(a) $C_4H_{10} \rightleftarrows C_4H_8 + H_2$

(b) $C_4H_{10} \rightleftarrows 0.1C_4H_8 + 0.1H_2 + 1.8$ (dealkylation products)

(c) $C_4H_8 \rightleftarrows 0.1H_2 + 1.8$ (dealkylation products)

Although the data were not conclusive, it was indicated that the rate of the principal reaction (a) is controlled by a surface reaction between adsorbed butane molecules and adjacent vacant active centers. On this basis the following equations were developed.

$$r_{ma} = \frac{C\left(p_A - \dfrac{p_R p_S}{K}\right)}{(1 + p_A K_A + p_{RS} K_{RS})^2} \tag{94}$$

where r_{ma} = rate of reaction, moles/(mass of catalyst) (hr)
C = over-all rate constant, moles/(mass of catalyst) (hr) (atm)
K = over-all gas-phase equilibrium constant, atm
K_A = effective adsorption equilibrium constant of butane, 1/atm
K_{RS} = effective average adsorption constant of hydrogen and butenes
p_{RS} = average partial pressure of hydrogen and butene = $(p_R + p_S)/2$.

The constants are related to temperature (T°K) by the following equations:

$$\log C = -\frac{36{,}000}{4.575\,T} + 8.1532 \tag{95}$$

$$\log K_A = \frac{18{,}073}{4.575T} - 5.0273 \tag{96}$$

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[19] R. H. Dodd and K. M. Watson, *Trans. Am. Inst. Chem. Engrs.*, **42**, 263 (1946). Also "Principles of Reactor Design," National Petroleum Publishing Company, Cleveland (1946).

$$\log K_{RS} = \frac{20{,}092}{4.575T} - 5.0273 \tag{97}$$

$$\log K = \frac{-28{,}800}{4.575T} + 6.7532 \tag{98}$$

The cracking reactions (b) and (c) were assumed to follow the following equation:

$$r_{mb} = kp_A; \qquad r_{mc} = kp_R \tag{99}$$

where

r_{mb} and r_{mc} = rates of reactions (b) and (c), respectively, moles/(mass of catalyst) (hr)

p_A, p_R = partial pressures of butane and butene, respectively

k = apparent reaction velocity constant

$$\log k = \frac{-73{,}900}{4.575T} + 16.43 \tag{100}$$

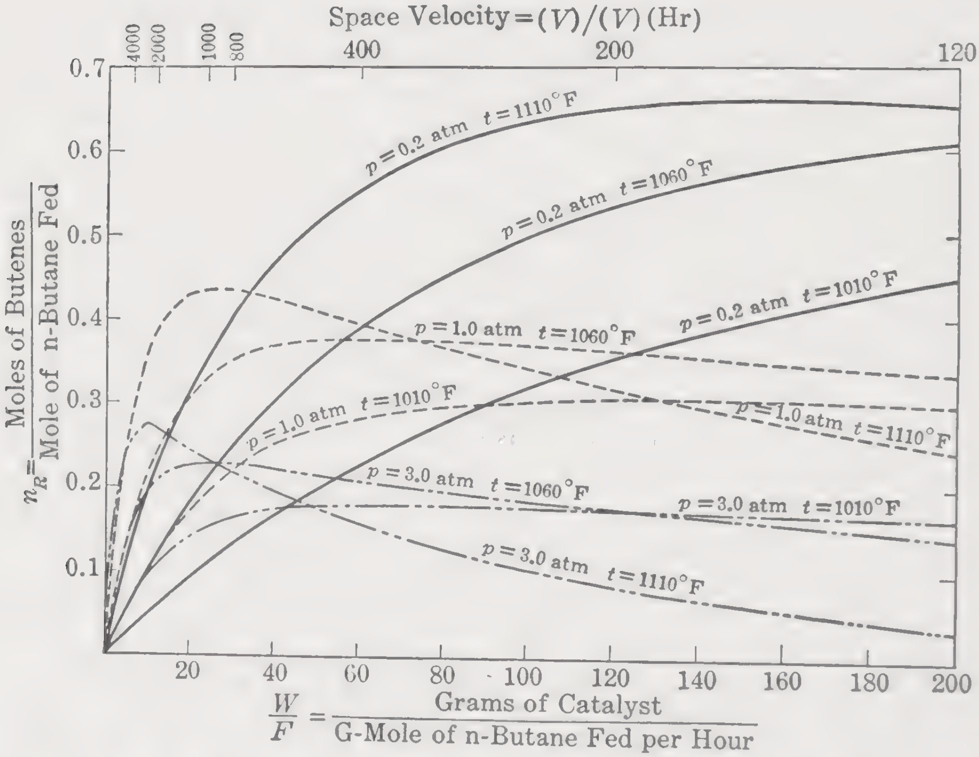

Fig. 192. Butene Production by the Catalytic Dehydrogenation of *n*-Butane.

The results of simultaneously integrating Equations (94) and (99) for selected isobaric–isothermal reactors are shown in Figs. 192 and 193. These integrations were carried out by the progressive stepwise procedure demonstrated in Chapter XVIII which is equally applicable to conditions of varying temperature and pressure. In Fig. 192 it may be seen that the yield of butenes per mole of butane fed tends to pass through a maximum as space velocity is reduced. This maximum shifts with temperature and pressure in a complex fashion. Similarly, in Fig. 193 it is seen that the selectivity of the operation follows a complicated pattern with low temperatures most favorable at low conversions, whereas the reverse is true at high conversions.

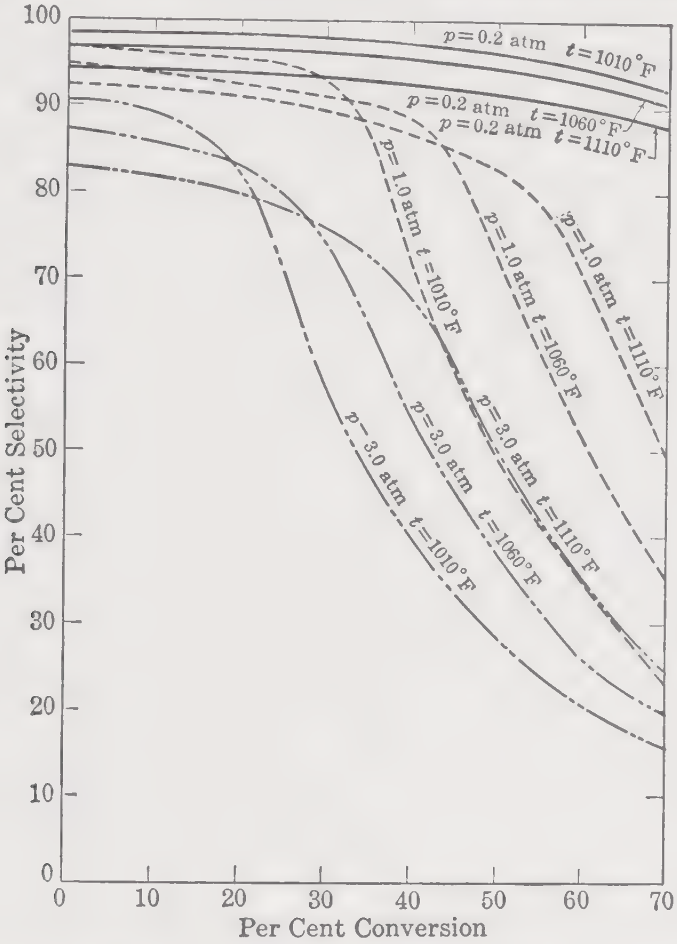

FIG. 193. Selectivity in the Catalytic Dehydrogenation of *n*-Butane.

Because of the several admittedly unsound assumptions involved in the development of Equations (94–100), it is probable that the relationships of Figs. 192 and 193 are not very accurate. However, it is believed that the trends are qualitatively correct. It is of interest that so complete a pattern can be developed from only a few experimental runs. It would be extremely difficult to evaluate the trends shown in the lower conversion range of Fig. 193 by experimentation alone.

More complete evaluations and more complex systems require more data than were used for Equations (94–100). Such data are preferably of the differential type, but frequently difficulties of chemical analysis interfere, and integral conversions must be determined.

PROBLEMS

1. The equilibrium constant for the chemisorption of a gas A without dissociation on a catalytic surface is 10.0 with activities referred to partial pressures in atmospheres. The number of molal adsorption sites L, corresponds to 0.5 g-mole per kg of catalyst.

(*a*) Plot a curve relating the equilibrium concentration of the adsorbed gas A in gram-moles per kilogram as a function of partial pressure over the range of 0–10 atm, assuming that no other component is adsorbed.

(*b*) Replot the curve of part (*a*) for the adsorption of gas A from a mixture containing 40 mole per cent of A and 60 mole per cent of component B which has an adsorption equilibrium constant of 5.0.

(*c*) Replot the curve of part (*b*) for the case in which the partial pressure of component B is held constant at 2.0 atm and the partial pressure of A is varied from 0 to 10 atm.

2. Repeat problem 1 for the case in which component A is dissociated on adsorption into two $\frac{1}{2}A$ atoms.

3. Develop derivations for the following rate equations in Chapter XIX:

a (42)	*b* (43)	*c* (44)
d (45)	*e* (46)	*f* (47)

4. Derive the following equations of Table LVII:

a (a)	*b* (b)	*c* (c)

5. From the following experimental data relating j factors for mass transfer and modified Reynolds numbers D_pG/μ, establish the best value of constants a and b in the relationship, $j = a\left(\frac{D_pG}{\mu}\right)^b$, using the method of least squares.

j	D_pG/μ	j	D_pG/μ
0.0928	332	0.0636	970
0.0840	493	0.0538	1160
0.0690	595	0.0536	1371
0.0693	734	0.0482	1555
0.0662	809	0.0453	1655
0.0637	914	0.0476	1858

6. From the data in Table A of Illustration 2 evaluate by the method of least squares the constants of the rate equation corresponding to mechanism d at a temperature of 275°C.

7. Toluene is produced in accordance with Equation (68) by passing an equimolal mixture of benzene and xylenes over a catalyst at a temperature of 450°C. The catalyst has a bulk density of 45 lb per cu ft. In order to investigate the kinetics of the reaction pilot plant runs were made at the conditions summarized in Table A. In all cases the process periods were so short that fouling of the catalyst may be neglected. The equilibrium constant of the reaction at this temperature may be taken as 3.5. Assuming that the rate equation is of the form of Equation (69):

$$r = \frac{C(a_A a_B - a_R^2/K)}{(1 + a_A K_A + a_B K_B + a_R K_R)^2}.$$

(*a*) Graphically evaluate the initial rates of toluene production in lb-moles/(hr) (lb) at zero conversion for the various pressures of operation.

Compare the results obtained by measuring the slopes of the origins of the curves relating x to W/F with those obtained by plotting a curve relating $x/(W/F)$ to W/F and extrapolating to $W/F = 0$.

(*b*) From the results of part (*a*) evaluate the constants $(K_A + K_B)$ and C of Equation (69), using the method of least squares. Activities should be referred to unit fugacity in atmospheres.

(*c*) Determine the differential-reaction rates corresponding to various degrees of conversion by plotting and graphically differentiating the data at 465 lb per sq in. Conversions expressed in moles of toluene per mole of feed should be plotted as ordinates against W/F (lb) (hr) /lb-mole and values of r evaluated at abscissas of 50, 75, 100, 125, and 150.

(*d*) Using the values of C and $(K_A + K_B)$ determined in part (*b*) evaluate the arithmetic average K_R corresponding to the differential rates of part (*c*).

(*e*) Verify the value of K_R determined in part (*d*) by plotting calculated values of $1/r$ as ordinates against x as abscissas and graphically integrating to establish the relationship between x and W/F for comparison with the experimental values.

(*f*) Using Equation (e) of Table LVII evaluate the constant K_R from the data at a pressure of 465 lb per sq in. and space velocities of 1.0 and 0.5. Compare the average of these values with that of part (*d*).

(*g*) Using the constants determined in parts (*b*) and (*f*) in Equation (e) of Table LVII, plot a curve relating x to W/F for comparison with the data of Table A for a pressure of 465 lb/sq in.

TABLE A

Pressure, lb per sq in.	S_l, *1/hr*	*Toluene, Mole Per Cent*	*Pressure, lb per sq in.*	S_l, *1/hr*	*Toluene, Mole Per Cent*
20	0.5	4.5	315	3.0	10.7
20	0.25	8.3	315	6.0	5.6
65	1.0	12.5	465	6.0	5.9
65	2.0	6.6	465	3.0	11.0
115	2.0	8.6	465	1.0	26.5
115	4.0	4.4	465	0.5	35.0

S_l = liquid hourly space velocity referred to 60°F.

8. Dodd and Watson[19] found the following relationship between butene production and space velocity in the catalytic dehydrogenation of n-butane at a temperature of

1060°F and a pressure of 1.0 atm.:

Butene produced, moles per mole fed	W/F *(lb catalyst) (hr)/lb-mole butane*
0.05	1.0
0.10	3.2
0.17	8.1
0.22	11.5
0.27	16
0.34	32

The equilibrium constant of the dehydrogenation reaction at this temperature may be taken as 0.2 atm.

(*a*) Plot these data on charts of the type of Figs. 190 and 191.

(*b*) Determine the error which would result in estimating the conversion where $W/F = 5$ and 30, respectively, by assuming that this complex reaction follows a conversion–space-velocity relationship of a pseudo-first-order form based on the experimental point at 25 per cent conversion.

9. Assuming the applicability of Equations (94–100) calculate the initial selectivity obtained at zero conversion in the dehydrogenation of *n*-butane to butene at the following conditions of temperature and pressure.

(*a*) 3.0 atm, 1100°F
(*b*) 1.0 atm, 1100°F
(*c*) 0.3 atm, 1100°F
(*d*) 1.0 atm, 1150°F
(*e*) 1.0 atm, 1050°F

CHAPTER XX

MASS AND HEAT TRANSFER IN CATALYTIC BEDS

The reaction rate equations developed in the preceding chapter all involve activities or partial pressures of the reacting components at the surface of the catalyst. As previously pointed out, these interfacial activities may be significantly different from the average activities of the main fluid stream because of the gradients required for the diffusion of reactants toward and products away from the interface. These activity differences due to diffusion may be neglected under conditions of relatively slow reaction rates combined with favorable conditions for mass transfer such as result from high velocities of flow and from small particles. In general, the calculation of heterogeneous reaction rates should include evaluation of the diffusional gradients of the system.

A further complication in heterogeneous catalytic rate calculations is introduced by heat transfer. Since the actual reaction occurs on the surface, the heat of reaction is absorbed or released at this point, and temperature differences exist between the reaction surface and the fluid. Where thermal effects are large, the control of temperature by suitable heat-transfer arrangements becomes the most important problem of reactor design.

Since the transfer of mass and heat are closely related phenomena of great importance in heterogeneous reactions, these principles are developed concurrently in considerable detail.

Laminar and Turbulent Flow. It has been experimentally demonstrated that when a fluid flows at low velocities over the surface of a solid or the interface of another immiscible fluid, the flow tends to be laminar. At the interface the velocity relative to the other phase is substantially zero while at increasing distances from the interface the velocity progressively increases. In effect the fluid may be considered as composed of thin layers which follow the contours of the surface without mixing with the adjacent layers except as mingling results from molecular diffusion. Even in laminar motion the flow is not necessarily linear but follows the contours of the restraining surfaces as though a bundle of silk filaments or ribbons were being pulled over the surface, each maintaining its same relative position, regardless of the irregularity of the path. In fluids flowing around bends in pipes laminar flow may take a spiral path not conforming to the shape of the bend. Laminar flow is also referred to as *viscous* or *streamline.*

If the velocity of laminar flow is increased, a condition is finally reached at which mixing of the adjacent layers of fluid begins and cross-flow currents and eddies are established in the moving stream. The velocity at which such cross currents and turbulence are established is termed the *critical velocity* marking the transition from laminar to what is termed *turbulent* flow. For isothermal flow in a path of uniform cross section such as in a pipe the critical velocity is sharply defined, whereas in flow through irregular passages as in a bed of granular material the transition from laminar to turbulent flow occurs gradually over a range of velocities. Also in nonisothermal flow when heat is being transferred through a fluid stream a gradual transition from laminar to turbulent flow results because of mixing induced by thermal convection.

The Film Concept. Even under conditions of turbulent flow there is always a layer of fluid at the interface in which laminar flow is maintained. The thickness of this laminar layer or *film* depends upon the conditions of flow, and becomes less as the velocity is increased. At sufficiently low velocities laminar flow may include the entire stream. The term film as used in fluid flow should not be confused with adsorbed films which may be only a single molecule in thickness.

For engineering problems dealing with mass and heat transfer in turbulent fluid streams it has proved convenient to assume that conditions of concentration and temperature are uniform in the main body of the stream and that the differences between the average conditions of the stream and those at the interface all occur across an effective boundary film. Actually small fractions of the total gradients of concentration and temperature occur in the turbulent zone so that the effective film thickness represents an arbitrary extension of the actual laminar layer to include the entire gradient. For this reason the effective thickness of the film may be slightly different for heat transfer than for mass transfer.

On the basis of this *film concept* mass transfer is considered as resulting from molecular diffusion across the effective film under the influence of a concentration gradient. Similarly, heat transfer is considered as taking place by thermal conduction through the film as a result of a difference in temperature between the interface and the average temperature of the fluid stream.

More detailed general discussions of fluid flow, heat transfer, and mass transfer are to be found in the standard texts on unit operations, absorption,[1] and heat transmission.[2]

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[1] T. K. Sherwood, "Absorption and Extraction," McGraw-Hill Book Company, New York (1937).

[2] W. H. McAdams, "Heat Transmission," McGraw-Hill Book Company, New York (1942).

DIFFUSION

If two gases A and B at the same pressure are initially separated into two adjoining compartments, removal of the partition will initiate transfer of component A into B and B into A by diffusion. The theory of diffusion in gases is based chiefly on kinetic theory and was developed principally by Maxwell[3] and Stefan.[4] A summarized discussion is presented by Sherwood,[1] and a more extensive development is given by Jeans.[5]

According to the classical kinetic theory of gases the diffusion of component A in a gaseous mixture of components A and B results from a driving force which is equal to the partial pressure or concentration gradient $-dp_A/dL$ which exists at any instant in the direction of diffusion. This driving force is expended in overcoming a resistance to diffusion which is proportional to the product of the concentration of the gases. Mathematically,

$$-\frac{dp_A}{dL} = \alpha_{AB}C_AC_B(u_A - u_B) = \alpha_{AB}\frac{n_An_B}{V^2}(u_A - u_B) \tag{1}$$

where p_A = partial pressure of A

L = distance in the direction of diffusion of A

α_{AB} = a proportionality factor

C_A, C_B = molal concentrations of A and B, respectively

u_A, u_B = linear velocities of diffusion of A and B in the direction of diffusion of A

Where the ideal-gas law is applicable, Equation (1) may be written

$$-\frac{dp_A}{dL} = \alpha_{AB}\frac{p_Ap_B}{(RT)^2}(u_A - u_B) \tag{2}$$

also

$$u_A = r_{Aa}v_A = \frac{r_{Aa}RT}{p_A} \tag{3}$$

where r_{Aa} = the molal rate of diffusion of A, in moles per unit time per unit of cross-sectional area of diffusional path.

v_A = molal volume of component A.

Substituting (3) in (2)

$$-\frac{dp_A}{dL} = \frac{\alpha_{AB}}{RT}(r_{Aa}p_B - r_{Ba}p_B) \tag{4}$$

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[3] J. C. Maxwell, *Sci. Papers*, **2**, p. 5, Cambridge University Press (1890).

[4] J. Stefan, *Sitzber. Akad. Wiss. Wien*, **63** (2), 63 (1871); **65** (2), 323 (1872).

[5] J. H. Jeans, "Dynamical Theory of Gases," 3d edition, Chapter XIII, Cambridge University Press (1921).

In the counterdiffusion of two components it follows that the two rates must be equal and opposite since the average molecular concentration and total pressure must be unchanged. Thus,

$$r_{Aa} = -r_{Ba} \tag{5}$$

$$p_A + p_B = \pi \tag{6}$$

Combining (5) and (6) with (4) and rearranging gives

$$r_{Aa} = -\frac{RT}{\alpha_{AB}\pi}\frac{dp_A}{dL} \tag{7}$$

or, since $p_A = C_A RT$,

$$r_{Aa} = -\frac{(RT)^2}{\alpha_{AB}\pi}\frac{dC_A}{dL} \tag{8}$$

Equation (8) forms the basis for the definition of the coefficient of diffusion D_{AB} of components A and B.

$$r_{Aa} = -r_{Ba} = -D_{AB}\frac{dC_A}{dL} = -\frac{D_{AB}}{RT}\frac{dp_A}{dL} \tag{9}$$

$$D_{AB} = \frac{(RT)^2}{\alpha_{AB}\pi} \tag{10}$$

Equation (9) is a fundamental equation for the diffusion of gases but is directly applicable only to a binary mixture of A and B in which equimolal counterdiffusion exists. It is evident that the diffusion coefficient D_{AB} is a physical constant having the dimensions of (length)^2/(time) which is characteristic of the *pair* of components A and B.

Unidirectional Diffusion in Binary Gas Mixtures. If a mixture of components A and B at constant pressure is brought into contact with an interface at which component A is removed from the gaseous phase but component B is not, diffusion of A will result and a concentration of B will be maintained in a stagnant film. Since diffusion of A requires a concentration gradient of A a similar gradient must exist for component B in order to meet the requirement of a uniform total pressure. Thus, $dC_A/dL = -dC_B/dL$.

Since, in the case under consideration, no component B is removed from or supplied to the interface under steady-state conditions it follows that the *net* rate of movement of B is zero with respect to the fixed point in space represented by the interface. However, the two components must maintain the diffusion velocities *relative to each other* which are called for by Equation (1). If velocities are expressed relative to the fixed interface, both u_B and r_B become zero, and Equation (4) becomes

$$-\frac{dp_A}{dL} = \frac{dp_B}{dL} = \frac{\alpha_{AB} p_B r_{Aa}}{RT} = \frac{RT}{D_{AB}\pi} p_B r_{Aa} \tag{11}$$

Rearranging and integrating between the limits L_1 and L_2 gives

$$r_{Aa} = \frac{D_{AB}\pi}{RT(L_2 - L_1)} \ln \frac{p_{B2}}{p_{B1}} = \frac{D_{AB}\pi(p_{B2} - p_{B1})}{RTB_G p_f} \tag{12}$$

where B_G = effective film thickness = $L_2 - L_1$
p_f = the logarithmic mean of p_{B2} and p_{B1} which is defined as

$$p_f = \frac{p_{B2} - p_{B1}}{\ln\left(\dfrac{p_{B2}}{p_{B1}}\right)} = (p_{B2} - p_{B1})_{lm} \tag{13}$$

Since $p_{B2} - p_{B1} = p_{A1} - p_{A2}$, Equation (12) may also be written

$$r_{Aa} = \frac{D_{AB}\pi}{RTp_f B_G}(p_{A1} - p_{A2}) \tag{14}$$

Equation (14) is the fundamental form for unidirectional diffusion of component A through a stagnant film of component B.

Diffusion in Complex Systems. In heterogeneous chemical reactions two or more components may diffuse to and from an interface in the presence or absence of a film of inert gas. The transfer may be equimolal in both directions or may correspond to an increase or decrease in the number of moles.

Gilliland[1] has developed a rigorous treatment of the simultaneous diffusion of two gases in the presence of a stagnant film which leads to complex equations for even this relatively simple case. However, useful approximations are obtained by simple relationships which are based on the assumption that, in a complex system of diffusing gases, the diffusional gradient established for any component A is equal to the sum of the gradients which would result from the separate diffusion of A with each of the other components in separate binary systems in which the concentrations and rate are the same as the complex system.

For the general gaseous reaction, $aA + bB \rightleftarrows rR + sS$ proceeding in contact with a solid catalyst in the presence of an inert gas I, Equation (1) may be expanded on this basis to include the effect of all components present. Thus, for the diffusion of A,

$$-\frac{dp_A}{dL} = \alpha_{AB}C_A C_B(u_A - u_B) + \alpha_{AR}C_A C_R(u_A - u_R) + \alpha_{AS}C_A C_S(u_A - u_S) + \alpha_{AI}C_A C_I(u_A) \tag{15}$$

or, in the form of Equation (4) combined with (10),

$$-\frac{\pi}{RT}\frac{dp_A}{dL} = \frac{1}{D_{AB}}(r_{Aa}p_B - r_{Ba}p_A) + \frac{1}{D_{AR}}(r_{Aa}p_R - r_{Ra}p_A) + \frac{1}{D_{AS}}(r_{Aa}p_S - r_{Sa}p_A) + \frac{1}{D_{AI}}r_{Aa}p_I \qquad (16)$$

The terms u_I and r_I do not appear since there is no net diffusion of inert gas.

Because of the uncertainty of the proportionality factors α and the corresponding diffusivities in mixtures of several components and because of the complications resulting in attempting to apply different values for each binary pair, an average diffusivity D_{Am} will be used to replace the separate values recorded in Equation (16). The average value of the diffusion coefficient will be taken as the weighted mean of the values for each pair. Thus, for component A,

$$(1 - N_A)\,D_{Am} = N_B D_{AB} + N_R D_{AR} + N_S D_{AS} + N_I D_{AI} \qquad (17)$$

where $N_A, N_B \cdots$ = average mole fractions of components $A, B \cdots$ *in the diffusional film*

From the stoichiometry of the general reaction,

$$r_{Ba} = \left(\frac{b}{a}\right) r_{Aa}; \qquad r_{Ra} = -\left(\frac{r}{a}\right) r_{Aa}; \qquad r_{Sa} = -\left(\frac{s}{a}\right) r_{Aa} \qquad (18)$$

Substituting Equation (18) in (16) and replacing each diffusion coefficient with the average value D_{Am} gives

$$-\frac{\pi}{RT}\frac{dp_A}{dL} = \frac{1}{D_{Am}} r_{Aa}\left[p_B + p_R + p_S + p_I - p_A\frac{(b - r - s)}{a}\right] \qquad (19)$$

or, since $\pi = p_A + p_B + p_R + p_S + p_I$,

$$r_{Aa}dL = -\frac{D_{Am}\pi}{RT}\left[\frac{dp_A}{\pi - p_A\left(\dfrac{a + b - r - s}{a}\right)}\right] = -\frac{D_{Am}\pi}{RT}\left(\frac{dp_A}{\pi + p_A\delta_A}\right) \qquad (20)$$

where

$$\delta_A = \frac{r + s - a - b}{a}$$

Integrating between the film boundaries L and L_i, corresponding to an effective film thickness B_G gives

$$r_{Aa} = \frac{D_{Am}\pi}{RTB_G}\left(\frac{1}{\delta_A}\right) \ln \left(\frac{\pi + p_A\delta_A}{\pi + p_{Ai}\delta_A}\right) \tag{21}$$

Equation (21) also may be written in the form of Equation (14):

$$r_{Aa} = \frac{D_{Am}\pi}{RTB_G p_f}(p_A - p_{Ai}) \tag{22}$$

where

$$p_f = \frac{(\pi + \delta_A p_A) - (\pi + \delta_A p_{Ai})}{\ln \left(\dfrac{\pi + \delta_A p_A}{\pi + \delta_A p_{Ai}}\right)} \tag{23}$$

Equation (23) may be recognized as the logarithmic mean value of $(\pi + \delta_A p_A)$ over the boundary limits of the gas film. Thus, for diffusion of A,

$$p_f = [\pi + \delta_A p_A]_{lm} \tag{24}$$

Similarly, for S

$$p_f = [\pi - \delta_S p_s]_{lm} \tag{25}$$

where
$$\delta_S = \frac{r + s \cdots - a - b - \cdots}{s}$$

Where the ratio of $(\pi + \delta_A p_A)/(\pi + \delta_A p_{Ai})$ is small, for example, less than 1.2, the arithmetic mean is in close agreement with the logarithmic mean and may be used for most purposes.

For equimolal diffusion it may be recognized from Equation (24) that $p_f = \pi$ and Equation (22) reduces to the form of Equation (9). For the diffusion of only one component in the presence of a stagnant gas δ_A in Equation (23) is equal to -1, and the value of p_f becomes that given by Equation (13).

Equations (22) and (23) also can be applied where multicomponent diffusion takes place without stoichiometric relations. For example, in the countercurrent adsorption of one gas and desorption of another the constants a and s may be taken as the actual molal rates of adsorption and desorption, respectively, and the ratio $(s - a)/a$ may assume any value. Equation (15) indicates that for a given concentration gradient the rate of diffusion of A is favored by the presence of another component diffusing in the same direction and retarded by another component diffusing in the opposite direction. Approximate relative values of a and s may be obtained in such a case by calculating the rate at which each component would diffuse under the conditions of the system if the other were absent. This procedure is demonstrated in the following illustration:

Illustration 1. Sherwood[1] presents an illustration in which ammonia is diffusing from an air–ammonia mixture into water under a total pressure of 0.2 atm. The stagnant gas layer is assumed to be at 55°C. At a given point in the apparatus the partial pressure of water and ammonia in the main gas stream are respectively zero and 0.006 atm. The partial pressure of ammonia in the solution is considered as zero. The vapor pressure of water at 55°C is 0.0727 atm. The diffusion coefficients are given as follows:

D_{AB}, ammonia in air = 1.075 cm²/sec
D_{SB}, water vapor in air = 1.245 cm²/sec
D_{AS}, ammonia in water vapor = 1.47 cm²/sec

It is desired to calculate relative values of (*a*) the rate of diffusion of ammonia, neglecting the effect of the diffusion of water; (*b*) the rate of diffusion of water, neglecting the effect of the diffusion of ammonia; (*c*) the approximate rates of diffusion of water and ammonia, in the presence of each other.

(*a*) If the air and water are considered as a stagnant component B, the diffusion of ammonia is expressed by Equation (14) where $p_f = (0.2 - 0.194)/\ln(0.2/0.194) = 0.197$. Thus,

$$r_{Aa}RTB_G = (1.075)(0.2/0.197)(0.006) = 0.00655$$

(*b*) If the air and ammonia are considered as a stagnant component, the diffusion of water is similarly expressed by Equation (14) with $p_f = (0.2 - 0.1273)/\ln(0.2/0.1273) = 0.1609$.

$$r_{Sa}RTB_G = (1.245)(0.2)/(0.1609)(-0.0727) = -0.1125$$

(*c*) The arithmetic mean composition of the gas film in mole fractions is: $NH_3 = 0.015$; $H_2O = 0.182$; air = 0.803. The average diffusion coefficients of ammonia, D_{Am}, and water, D_{Sm}, are calculated from Equation (17) using this mean composition:

$$D_{Am} = \frac{(0.803)(1.075) + (0.182)(1.47)}{(1 - 0.015)} = 1.148$$

$$D_{Sm} = \frac{(0.803)(1.245) + (0.015)(1.47)}{(1 - 0.182)} = 1.249$$

The values of p_f are obtained from Equations (24) and (25) by using for a and s the values of r_{Aa} and $-r_{Sa}$ calculated for the individual diffusion of the components in binary systems.

For ammonia: $p_A = 0.006$; $p_{Ai} = 0$

$$(a - s)/a = (0.00655 - 0.11251)/(0.00655) = -16.18$$
$$\pi - p_A(a - s)/a = 0.2 + (0.006)(16.18) = 0.2971$$
$$p_f = (0.2971 - 0.2)/2.3026 \log(0.2971/0.2) = 0.2454$$

For water: $p_{Ai} = 0.0727$; $p_A = 0$

$$(s - a)/s = (0.11251 - 0.00655)/0.11251 = 0.94178$$
$$\pi - p_{Ai}(s - a)/s = 0.2 - (0.0727)(0.94178) = 0.13153$$
$$p_f = (0.2 - 0.13153)/2.3026 \log(0.2/0.13153) = 0.1634$$

The rates of diffusion of the two components in the presence of each other are obtained by substitution in Equation (22):

For ammonia:

$$r_{Aa}RTB_G = (1.148)(0.2/0.2454)(0.006) = 0.00561$$

For water:

$$r_{Sa}RTB_G = (1.249)(0.2/0.1634)(-0.0727) = -0.1111$$

By use of the more rigorous equations developed by Gilliland, Sherwood calculated values of 0.0057 and −0.1116 for these rates. The results of neglecting the effect of the diffusion of one gas in calculating the rate of diffusion of the other are summarized as follows for this illustration:

	Considering Counterdiffusion	*Neglecting Counterdiffusion*	*Percentage Error*
$r_{Aa}RTB_G$ (ammonia)	0.00561	0.00655	+16.7
$r_{Sa}RTB_G$ (water)	−0.1111	−0.1125	+ 1.3

Diffusion in the Liquid State. The rate of molecular diffusion of two components A and B in the liquid state is given by Fick's law which is analogous to Equation (9) for gases:

$$r_{Aa} = -D_{AB}\frac{dC_A}{dL} \tag{26}$$

where

r_{Aa} = rate of diffusion of A, moles/(area)(time)
C_A = concentration in moles per unit volume
D_{AB} = diffusion coefficient

Since

$$C_A = \frac{x_A}{v_m}$$

where

x_A = mole fraction
v_m = average molal volume of solution

Equation (26) becomes

$$r_{Aa} = -\frac{D_{AB}}{v_m}\frac{dx_A}{dL} \tag{27}$$

Equation (27) may be integrated over a film thickness B_L to give

$$r_{Aa} = \frac{D_{AB}}{v_m B_L}(x_A - x_{Ai}) \tag{28}$$

For the general case of diffusion in a complex system undergoing the reaction $aA + bB \rightleftarrows rR + sS$, a development analogous to that used for Equation (22) leads to

$$r_{Aa} = \frac{D_{Am}}{v_m B_L x_f}(x_A - x_{Ai}) \tag{29}$$

where x_f is the logarithmic mean value of the term, $(1 + \delta_A x_A)$ in the liquid film. For equimolal counterdiffusion, $x_f = 1.0$, and for the case of the unidirectional diffusion of A in a stagnant medium x_f is the logarithmic mean of the values of $(1 - x_A)$ at the film boundaries.

TRANSFER OF HEAT

The equations for the transfer of heat in fluid streams are similar in general form to those for diffusion and involve a parallel concept of a driving force, in this case a temperature difference, causing flow against a resistance concentrated in a fluid film. The heat-transfer problem is simplified by the fact that it may always be treated as a unidirectional single phenomenon. The basic equation of heat transfer may be written in the form of Equation (9).

$$q_a = -k\, dt/dL \tag{30}$$

or, in integrated form,

$$q_a = \frac{k(t_1 - t_2)}{L_2 - L_1} = \frac{k}{B_{hG}}(t_1 - t_2) \tag{31}$$

where q_a = heat-transfer rate per unit area
B_{hG} = effective film thickness for heat transfer
k = thermal conductivity Btu/(hr)(ft)(°F)

TRANSFER COEFFICIENTS, FACTORS, AND UNITS

The equations developed in the preceding section for diffusion and heat transfer are limited in their usefulness, because the value of the effective film thickness B is generally not known. For this reason it is convenient to group this term with the constants of the equations to form what are termed *transfer coefficients*. Thus, for the general case of mass transfer, Equation (22) may be written as

$$r_{Aa} = k_G(p_A - p_{Ai}) \tag{32}$$

where $k_G = \dfrac{D_{Am}\pi}{RTB_G p_f}$ = the mass-transfer coefficient of the gas film. An analogous expression may be written from Equation (29) in terms of k_L, the mass-transfer coefficient of the liquid film.

Similarly, for heat transfer, Equation (31) may be written as

$$q_a = h_G(t_1 - t_2) \tag{33}$$

where $h_G = k/B_{hG}$ = the heat-transfer coefficient of the gas film.

For the calculation of mass and heat transfer it is necessary that the transfer coefficients k_G, k_L, h_G, and h_L be empirically correlated in terms of the determining variables. These variables include the physical properties and conditions of the system which determine the diffusivities and thermal conductivity as well as the conditions of flow which determine the effective film thickness. In order to facilitate the plotting of experimental data for widely varying systems and conditions Colburn[6] and Chilton[7] combined dimensionless groups of the variables to define what they termed a *mass-transfer factor* j_d and a *heat-transfer factor* j_h.

$$j_d = \left(\frac{k_G M_m p_f}{G}\right)\left(\frac{\mu}{\rho D_{Am}}\right)_f^{\frac{2}{3}} \tag{34}$$

$$j_h = \left(\frac{h_G}{C_p G}\right)\left(\frac{C_p \mu}{k}\right)_f^{\frac{2}{3}} \tag{35}$$

where

k_G = mass-transfer coefficient of the gas film
M_m = mean molecular weight of the gas stream
p_f = film pressure factor, defined by Equation (23)
G = mass velocity, mass/(area)(time)
μ = viscosity of gas
ρ = density of gas
D_{Am} = average diffusivity of component A
$(\mu/\rho D_{Am})$ = the dimensionless Schmidt number
h_G = heat-transfer coefficient of the gas film
C_p = specific heat of the gas
k = thermal conductivity of the gas
$(C_p\mu/k)$ = the dimensionless Prandtl number
Subscript f = properties at average condition of the film

Equations (34) and (35) are also directly applicable to liquid films.

The mass- and heat-transfer factors have the advantage of correlating as unique functions of the dimensionless Reynolds number (DG/μ) in a form analogous to that of the correlation of the friction factor of the Fanning equation for pressure drop in fluid flow. Thus,

$$j_d = \phi\left(\frac{DG}{\mu}\right); \qquad j_h = \phi'\left(\frac{DG}{\mu}\right) \tag{36}$$

where

ϕ and ϕ' denote unique functions for a particular mechanical system of flow

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[6] A. P. Colburn, *Trans. Am. Inst. Chem. Engrs.*, **29**, 174 (1933).

[7] T. H. Chilton and A. P. Colburn, *Ind. Eng. Chem.*, **26**, 1183 (1935).

D = effective diameter of the path of fluid flow
G = mass velocity
μ = viscosity of the fluid
(DG/μ) = Reynolds number at the average conditions of the fluid stream

Chilton and Colburn pointed out that ϕ and ϕ' are numerically similar and that as an approximation for turbulent flow in a circular cylinder j_d may be taken as equal to j_h and to $f/2$ where f is the friction factor of the Fanning equation. These analogies lead to serious errors in other cases, and correlations based on measurements of the separate phenomena of interest are required.

Although the j transfer factors are most convenient for the correlation of experimental data they are somewhat cumbersome in application to process design and analysis problems. The basic transfer coefficients k_G and h_G are more convenient to use but have the disadvantage of varying over wide ranges with changes in mass velocity G, the film pressure factor p_f, and the specific heat C_p. For convenience of application in packed towers and granular beds Chilton and Colburn[8] developed a method of expressing the mass- and heat-transfer characteristics of a system in terms of the *height of a transfer unit* H_d or H_h. As its name implies, the height of a transfer unit has the dimension of length and is a measure of the height of packing or bed required for a specified transfer service. Accordingly it must vary inversely with the corresponding transfer coefficient. The physical significance of the *transfer unit* is developed on page 991. By definition,

$$H_{dG} = \frac{G}{k_G M_m p_f a_v} \tag{37}$$

$$H_{hG} = \frac{GC_p}{h_G a_v} \tag{38}$$

where

H_{dG} = height of gas-film mass-transfer unit
H_{hG} = height of gas-film heat-transfer unit
a_v = interfacial area per unit volume of packing or bed

Similar definitions may be applied to liquid films.

By combining (34) with (37) and (35) with (38):

$$a_v H_{dG} = \frac{1}{j_d}\left(\frac{\mu}{\rho D_{Am}}\right)_f^{\frac{2}{3}} = \frac{G}{k_G M_m p_f} \tag{39}$$

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[8] T. H. Chilton and A. P. Colburn. *Ind. Eng. Chem.*, **27**, 255 (1935).

$$a_v H_{hG} = \frac{1}{j_h}\left(\frac{C_p\mu}{k}\right)_f^{\frac{2}{3}} = \frac{GC_p}{h_G} \tag{40}$$

Rates of heat and mass transfer in gases flowing through beds of uniformly sized granular solids were investigated by Gamson, Thodos, and Hougen[9] and by Wilke and Hougen.[10] These investigators correlated heat and mass-transfer factors j_h and j_d against a modified Reynolds number in which the diameter term is taken as the diameter of a sphere which has the same surface area as an average particle in the bed.

Thus,

$$D_p = \sqrt{a_p/\pi} \tag{41}$$

where

a_p = average surface area per particle

For cylinders of height and diameter each equal to D, Equation (41) reduces to

$$D_p = D\sqrt{1.5} \tag{42}$$

For spherical particles of diameter D or for cylinders whose height and diameter are each equal to D the surface area per unit volume is represented by the following equation:

$$a_v = \frac{6\rho_b}{\rho_p D} = \frac{6(1 - F_e)}{D} \tag{43}$$

where

ρ_b = bulk density of catalyst bed, mass/volume
ρ_p = actual density of catalyst particle, mass/volume
F_e = fraction of external void volume in catalyst bed

On this basis, Gamson, Thodos, and Hougen developed the following expression for j_h and j_d in the range of Reynolds numbers above 350:

$$\left.\begin{aligned} j_d &= 0.99(D_pG/\mu)^{-0.41} \quad (44)\\ j_h &= 1.06(D_pG/\mu)^{-0.41} \quad (45)\end{aligned}\right\} \quad (D_pG/\mu) > 350$$

Wilke and Hougen recommended the following equations for Reynolds numbers less than 350.

$$\left.\begin{aligned} j_d &= 1.82(D_pG/\mu)^{-0.51} \quad (46)\\ j_h &= 1.95\,(D_pG/\mu)^{-0.51} \quad (47)\end{aligned}\right\} \quad (D_pG/\mu) < 350$$

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[9] B. W. Gamson, G. Thodos, and O. A. Hougen, *Trans. Am. Inst. Chem. Engrs.*, **39**, 1 (1943).

[10] C. R. Wilke and O. A. Hougen, *Trans. Am. Inst. Chem. Engrs.*, **41**, 445 (1945).

where

G = mass velocity of flow based on the total cross-sectional area of the bed
D_p = effective diameter of particle from Equation (41)

No significance is attached to the value of D_pG/μ at 350. The mass- and heat-transfer factors form a smooth and continuous curve over the entire range of values, but for convenience the relationship may be expressed on logarithmic paper by two straight lines which intersect at 350.

For convenience in use, the relationships expressed by Equations (44) and (46) are combined with Equation (39) and plotted in Fig. 194 which shows values of a_vH_{dG} as a function of the modified Reynolds and the Schmidt numbers. Values of $(a_vH_{hG}/1.07)$ may also be read as ordinates from the chart by substituting the Prandtl number for the Schmidt number.

Equations (44–47) and Fig. 194 are based on data for the vaporization of water from completely wetted spherical and cylindrical particles of various materials ranging in diameter from 0.09 to 0.74 in. It is believed, however, that they may be applied to general problems of mass and heat transfer in gaseous systems at widely varying conditions if reliable values for the various physical constants are available.

No similar data are as yet available for heat and mass transfer in liquids flowing through granular beds. It seems reasonable to expect that relationships of the form of Equations (44) to (47) should represent this case, and in lieu of direct data it may be assumed that these equations are applicable to the liquid state.

For the calculation of diffusional pressure and temperature differences, from transfer unit data, Equations (39) and (40) may be combined with (32) and (33). Thus, if $\Delta p_A = p_{Ai} - p_A$, it follows that,

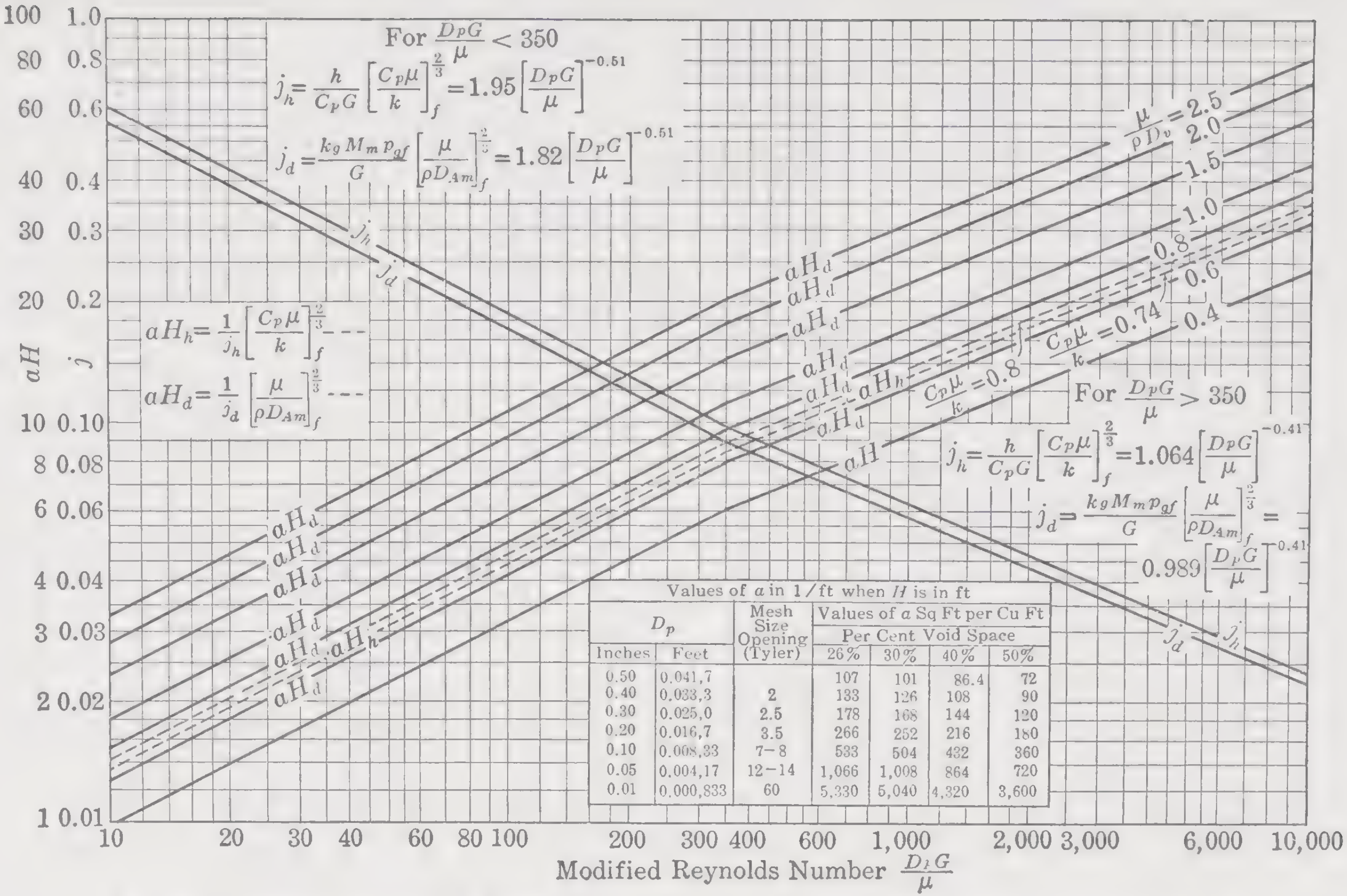
$$\Delta p_A = -\frac{r_{Aa}}{k_G} = -\frac{r_A}{k_G a_m} = -\frac{r_A \rho_B M_m p_f}{a_v G}(a_v H_{dG}) \tag{48}$$

Similarly, if $\Delta t = t_i - t$, it follows that

$$\Delta t = -q_m/h_G a_m = -\frac{r_A \rho_B \Delta H_A}{a_v G C_p}(a_v H_{hG}) \tag{49}$$

where

r_A = rate of reaction or mass transfer of A per unit mass of catalyst
q_m = rate of heat transfer per unit mass of catalyst
a_m = particle area per unit mass of catalyst
a_v = particle area per unit volume of catalyst bed = $a_m\rho_B$
ΔH_A = heat of reaction per mole of A reacted



Values of a in 1/ft when H is in ft

D_p		Mesh Size Opening (Tyler)	Values of a Sq Ft per Cu Ft			
			Per Cent Void Space			
Inches	Feet		26%	30%	40%	50%
0.50	0.041,7		107	101	86.4	72
0.40	0.033,3	2	133	126	108	90
0.30	0.025,0	2.5	178	168	144	120
0.20	0.016,7	3.5	266	252	216	180
0.10	0.008,33	7–8	533	504	432	360
0.05	0.004,17	12–14	1,066	1,008	864	720
0.01	0.000,833	60	5,330	5,040	4,320	3,600

FIG. 194. Values of j and aH for Mass and Heat Transfer in Gases Flowing Through Granular Solids.

(Reproduced in " C.P.P. Charts ")

PHYSICAL CONSTANTS

In order to use Fig. 194 or Equations (44–47) for the evaluation of transfer data it is necessary that the physical constants ρ, C_p, μ, D_{Am}, and k be known for the system. Generalized methods for estimating the first three constants in the absence of experimental data are discussed in Chapters XII, XVII, and XVIII, respectively.

Diffusion Coefficient. The diffusion coefficient D_{AB} for the interdiffusion of two gases, A and B, may be estimated from the following empirical relationship developed by Gilliland:[11]

$$D_{AB} = 0.0043 \frac{T^{\frac{3}{2}}}{\pi(v_A^{\frac{1}{3}} + v_B^{\frac{1}{3}})^2} \sqrt{\frac{1}{M_A} + \frac{1}{M_B}} \qquad (50)$$

D_{AB} = diffusion coefficient, cm²/sec
T = temperature, degrees Kelvin
M_A, M_B = molecular weights of A and B
π = total pressure, atmospheres
v_A, v_B = molecular volumes of A and B which may be taken from Table LIX for simple gases or estimated as the sum of the indicated atomic volumes for complex molecules

TABLE LIX

ATOMIC VOLUMES FOR COMPLEX MOLECULES

Bromine	27.0	Oxygen in:	
Carbon	14.8	Aldehydes and ketones	7.4
Chlorine	24.6	Methyl esters	9.1
Hydrogen	3.7	Methyl ethers	9.9
Iodine	37.0	Higher esters and ethers	11.0
Nitrogen, double-bonded	15.6	Acids	12.0
In primary amines	10.5	Sulfur	25.6
In secondary amines	12.0		
In aromatic compounds deduct:			
For benzene ring	15		
For naphthalene ring	30		
Molecular volumes of simple gases:[12]			
H_2	14.3	NH_3	25.8
O_2	25.6	H_2O	18.9
N_2	31.2	H_2S	32.9
Air	29.9	COS	51.5
CO	30.7	Cl_2	48.4
CO_2	34.0	Br_2	53.2
SO_2	44.8	I_2	71.5
NO	23.6		
N_2O	36.4		

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[11] E. R. Gilliland, *Ind. Eng. Chem.*, **26**, 681 (1934).

[12] J. H. Arnold, *Ind. Eng. Chem.*, **22**, 1091 (1930).

Illustration 2. Calculate the diffusion coefficient of gaseous benzene in air at 80°C and 1 atm. From Equation (50) and Table LIX:

For benzene, $v = 6(14.8) + 6(3.7) - 15 = 96.$

$$D = 0.0043 \frac{(353.1)^{\frac{3}{2}}}{1.0(96^{\frac{1}{3}} + 29.9^{\frac{1}{3}})^2}\sqrt{\frac{1}{78} + \frac{1}{29}}$$

$$= 0.1051 \text{ sq cm per sec or } (0.1051)(3.87) = 0.407 \text{ sq ft per hr}$$

Experimentally determined diffusion coefficients for many systems of both gases and liquids are included in the International Critical Tables, Volume V. In general the coefficients for gases range from 0.05 to 10 sq cm per sec while those for liquids are much lower, generally falling in the range of 0.3 to $(5)10^{-5}$ sq cm per sec. An empirical method for the estimation of diffusion coefficients of liquids in the absence of experimental data was developed by Arnold.[13]

Thermal Conductivity. Few reliable data are available for the thermal conductivity k of fluids. The thermal conductivities of liquids are in general relatively little affected by temperature and fair approximations for many substances can be arrived at by study of tables[2] of experimental values for similar materials.

In heat-transfer equations for gases the thermal conductivity appears only as a part of the dimensionless Prandtl number $(C_p\mu/k)$. For ideal gases this number shows little variation with temperature, pressure, or type of gas. Prandtl numbers of various gases are given in Table LX for a temperature of 212°F and 1 atm. The effects of temperature and pressure are uncertain and in general may be neglected except in the critical region.

TABLE LX

PRANDTL NUMBERS OF GASES AT 212°F AND 1 ATM

	$\frac{C_p\mu}{k}$	$\left(\frac{C_p\mu}{k}\right)^{\frac{2}{3}}$
Air, CO, H_2, N_2, O_2	0.74	0.818
NH_3	0.78	0.848
CO_2, SO_2	0.80	0.862
Ethylene	0.83	0.883
H_2S	0.77	0.840
Methane	0.79	0.855
H_2O	0.78	0.848

Taken from "Heat Transmission," by W. H. McAdams, McGraw-Hill Book Company (1942), New York (with permission).

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[13] J. H. Arnold, *J. Am. Chem. Soc.*, **52**, 3937 (1930).

McAdams[2] recommends the following equation based upon the work of Maxwell and Eucken for estimating the value of the Prandtl number

$$\frac{C_p\mu}{k} = \frac{4}{9 - \dfrac{5C_v}{C_p}} \tag{51}$$

PROCESS RATES CONTROLLED BY DIFFUSION

Many processes in heterogeneous systems proceed at rates which are almost entirely determined by rates of mass and heat transfer through a single laminar film at the interface. This situation results when all reactions occurring at the interface proceed at such high rates that conditions of equilibrium may be assumed to exist. Heterogeneous reacting systems tend to approach this condition at high temperatures where the rates of chemical combination become very high without proportional increases in the rates of mass transfer which are little affected by temperature. In catalytic operations an analysis based on the assumption that the rate is controlled by mass transfer is frequently of interest as indicative of the minimum reactor size that may result from the ultimate in catalyst activity.

A useful general equation for such a process in which interfacial partial pressures may be assumed constant or may be calculated from equilibrium relationships may be derived by consideration of the general reaction $aA + bB \rightleftarrows rR + sS$ occurring in a gas stream flowing through a granular bed at substantially constant temperature and total pressure. In an elementary section of bed of thickness dZ and unit cross-sectional area the quantity of A transferred to the interface in a unit time must equal the quantity lost from the gas stream if steady-state conditions prevail. Expressing this material balance mathematically for ideal gas behavior,

$$k_{GA}a_v(p_A - p_{Ai})dZ = -d\left(\frac{p_A G}{\pi M_m}\right) \tag{52}$$

Before integration can be carried out it is necessary to express the molal rate of flow G/M_m in terms of p_A. The change in number of moles per mole of A reacting is expressed by $\delta_A = (r + s - a - b)/a$. Then, in terms of x_A, the moles of A reacting per mole of feed,

$$\frac{G}{M_m} = \frac{G}{M_{mo}}(1 + x_A\delta_A) \tag{53}$$

Also, since $x_A = n_{Ao} - n_A$ and $p_A = n_A\pi/(1 + x_A\delta_A)$,

$$x_A = \frac{p_{Ao}}{\pi} - \frac{p_A(1 + x_A\delta_A)}{\pi} \tag{54}$$

where the subscript o denotes the properties of the feed. Combining (52) and (54) and rearranging gives

$$\frac{G}{M_m} = \frac{G}{M_{mo}}\left(\frac{\pi + p_{Ao}\delta_A}{\pi + p_A\delta_A}\right) = \left(\frac{G}{M_{mo}}\right)\left(\frac{1 + p_{Ao}\delta_A/\pi}{1 + p_A\delta_A/\pi}\right) \tag{55}$$

Substituting (55) in (52) yields

$$\begin{aligned} dZ &= -\frac{G(1 + p_{Ao}\delta_A/\pi)}{M_{mo}\pi k_{GA}a_v}\,\frac{1}{(p_A - p_{Ai})}\,d\left(\frac{p_A}{1 + p_A\delta_A/\pi}\right) \\ &= -\frac{G(1 + p_{Ao}\delta_A/\pi)}{M_{mo}\pi k_{GA}a_v}\,\frac{dp_A}{(p_A - p_{Ai})(1 + p_A\delta_A/\pi)^2} \end{aligned} \tag{56}$$

Replacing G/M_{mo} by its value from Equation (55) and introducing the film pressure factor p_f in both the numerator and denominator results in

$$dZ = -\frac{G}{M_m k_{GA} p_f a_v}\,\frac{p_f dp_A}{(\pi + p_A\delta_A)(p_A - p_{Ai})} \tag{57}$$

Equation (57) cannot be directly integrated for the general case but may be handled by an approximate graphical integration and averaging procedure which is satisfactory for many purposes. Thus, an integrated form may be written as follows:

$$Z_2 - Z_1 = -\left(\frac{G}{M_m k_{GA} p_f a_v}\right)_{\text{avg}} \int_{p_{A_1}}^{p_{A_2}} \frac{p_f dp_A}{(\pi + p_A\delta_A)(p_A - p_{Ai})} \tag{58}$$

The term inside the parenthesis of Equation (58) may be recognized as the height of a transfer unit H_{dG} defined by Equation (37). Although the terms M_m, k_{GA}, and p_f in this group all vary as functions of p_A or Z in a given reactor and properly should be included in the integral, the variation of the entire term is generally not large, and the arithmetic average of the terminal values at Z_1 and Z_2 may be used as a good approximation.

The integral of Equation (58) may be evaluated graphically by plotting p_A against $p_f/(\pi + p_A\delta_A)(p_A - p_{Ai})$. In simple cases where p_{Ai} is constant and p_f may be expressed as the arithmetic mean, analytical integration is possible. The value of this integral is a measure of the difficulty or duty of the transfer operation which is determined by the partial pressure change produced and the driving force causing it. Chilton and Colburn[8] have termed this integral the *number of transfer units* required for the operation. Where variations in the ratio $p_f/(\pi + p_A\delta_A)$ are small, it is evident that a single transfer unit produces a partial pressure change in the gas stream which is equal to the average driving force. With this concept Equation (58) may be written as

$$Z_2 - Z_1 = (H_{dG})_{\text{avg}} N_{dG} \tag{59}$$

where

$(H_{dG})_{\text{avg}}$ = average height of transfer unit

N_{dG} = number of transfer units

$$N_{dG} = \int_{p_{A_2}}^{p_{A_1}} \frac{p_f \, dp_A}{(\pi + p_A \delta_A)(p_A - p_{Ai})} = \int_{y_{A_2}}^{y_{A_1}} \frac{y_f \, dy_A}{(1 + y_A \delta_A)(y_A - y_{Ai})} \tag{60}$$

where y_A = mole fraction of A

$y_f = p_f/\pi$ = log mean of $(1 + y_A \delta_A)$ and $(1 + y_{Ai} \delta_A)$

Similar expressions may be derived for the liquid state.

By an analogous development equations for heat transfer may be obtained in the general forms of Equations (58–60). Thus,

$$Z_2 - Z_1 = -\left(\frac{GC_p}{h_G a_v}\right)_{\text{avg}} \int_{t_1}^{t_2} \frac{dt}{(t - t_i)} = H_{hG} N_{hG} \tag{61}$$

For the case of equimolal counterdiffusion, where $\delta = 0$, and $p_f = \pi$, Equation (58) reduces to

$$Z_2 - Z_1 = (H_{dG})_{\text{avg}} \int_{p_{A_2}}^{p_{A_1}} \frac{dp_A}{p_A - p_{Ai}} = (H_{dG})_{\text{avg}} \int_{p_{A_1}}^{p_{A_2}} \frac{dp_A}{\Delta p_A} \tag{62}$$

This situation is approximated in fractional distillation columns.

Evaluation of the integral of Equation (60) for the general case where the reverse reaction is of importance is complicated by uncertainty as to the value of p_{Ai}. When systems are dealt with in which the molecular weights of the reactants and products are not widely different and where p_f is not greatly different from π, the following approximate relationship may be assumed to exist between the partial pressure differences of the various components.

$$(p_{Ai} - p_A) = \Delta p_A = \Delta p_B \left(\frac{a}{b}\right) = -\Delta p_R \left(\frac{a}{r}\right) = -\Delta p_S \left(\frac{a}{s}\right) \tag{63}$$

Then, if equilibrium exists at the interface,

$$\Delta p_A = \left[\frac{\left(p_R - \Delta p_A \dfrac{r}{a}\right)^r \left(p_S - \Delta p_A \dfrac{s}{a}\right)^s}{K \left(p_B + \Delta p_A \dfrac{b}{a}\right)^b} \right]^{1/a} - p_A \tag{64}$$

In the general case Equation (64) may be solved graphically for Δp_A to correspond to selected values of p_A, and the corresponding values of p_B, p_R, and p_S which are determined by the stoichiometry of the system. The errors involved in use of Equation (64) are generally negligible if K is large but may become serious where gases of widely different characteristics are involved. In such cases the more rigorous stepwise integration discussed in the following section should be used.

Where p_f or y_f do not vary greatly they may be assumed to be constant at the arithmetic mean of the terminal values. Then, for cases where $y_{Ai} = 0$, Equation (60) reduces to

$$N_{dG} = (y_f)_{\text{avg}} \int_{y_{A_2}}^{y_{A_1}} \frac{dy_A}{(1 + y_A\delta_A)y_A} = (y_f)_{\text{avg}} \ln \left[\frac{y_{A1}(1 + y_{A2}\delta_A)}{y_{A2}(1 + y_{A1}\delta_A)}\right] \quad (65)$$

Illustration 3. A mixture of 38 mole per cent propylene and 62 mole per cent propane is charged to a vapor-phase catalytic polymerization reactor at a temperature of 450°F and an absolute pressure of 225 lb per sq in. The polymerization reaction is substantially unidirectional and produces a mixture of olefins having an average molecular weight of 105, an average boiling point of 220°F, and a specific gravity of 0.71 at 60°F. The catalyst is in the form of $\frac{1}{4} \times \frac{1}{4}$-in. cylinders with 50 per cent external voids. Assuming that the catalytic activity is so great that the concentration of propylene is zero at the interface, calculate the space velocity (per hour) required for 98 per cent polymerization of the propylene at a mass velocity of 200 lb/(hr)(sq ft).

The effects of variations in pressure throughout the reactor may be neglected.

Solution: The reaction under consideration is represented stoichiometrically by the equation:

$$2.5C_3H_6 \rightleftarrows C_{7.5}H_{15}$$

Basis: 100 lb-moles of feed, 98 per cent conversion of propylene.

Entering		*Leaving*		
Propylene	38 moles	Propylene	0.76 mole;	1.0%
Propane	62 moles	Propane	62.00 moles;	79.8%
		Polymer	14.90 moles;	19.2%

The temperature of the stream leaving the reactor may be calculated by the methods of Chapter VIII. However since temperature has relatively little effect on diffusional rates an approximate calculation is satisfactory in which the heat of reaction is assumed independent of temperature and the specific heat of the reactant stream taken as constant at that of the feed. The standard heat of reaction may be estimated from the group contributions of Table XL, page 759, if the polymer is assumed to have the properties of an equimolal mixture of 2,3-dimethyl butene-1 and 2,3,3,4-tetramethyl pentene-1.

Heats of formation	k-cal per g-mole
Propylene	+ 5.4
2,3-dimethyl butene-1	−15.2
2,3,3,4-tetramethyl pentene-1	−32.8

Heat of reaction, $\Delta H°$k-cal per g-mole propylene $= [(-15.2 - 32.8)0.5 - (2.5)5.4]/2.5 = -11.76$

$$\Delta H°\text{, Btu per lb-mole propylene} = -(15{,}000)(1.8) = -27{,}000$$

The molal heat capacity of the feed at 1000°R is calculated from Table XXI, page 336.

Propane	29.39
Propylene	24.41

$$\text{Feed} = (0.38)(29.39) + (0.62)(24.41) = 26.30$$

Approximate temperature rise $= (27{,}000)(0.38)(0.98)/26.30 = 382°\text{F}$
Approximate outlet temperature $= 832°\text{F}$
From Equation (42),

$$D_p(\text{ft}) = (0.25/12)(1.225) = 0.0225$$

From Equation (43),

$$a_v(1/\text{ft}) = \frac{(0.5)(6)(12)}{(0.25)} = 144$$

Physical Properties of Components

	Propane	*Propylene*	*Polymer*
Critical temperature T_c, °R	666 (Table XXVIII)	658 (ICT)	984 (Eq. III-14)
Critical pressure p_c, lb per sq in.	642 (Table XXVIII)	661 (ICT)	390 (Eq. III-15)
Critical viscosity μ_c, micropoises (Table LV)	228	233	259 (Fig 109)
Molecular weight	44	42	105
Molecular volume (Table LIX)	74.0	66.6	166.5

Physical Properties of Mixture

	Entering	*Leaving*
Pseudocritical properties		
Temperature, T_c'°R	663.5	727
Pressure, p_c', lb per sq in.	650	593
Viscosity, μ_c', micropoises	230	233
Pseudoreduced properties		
Temperature, T_r'	1.371	1.78
Pressure, p_r'	0.35	0.380
Viscosity (Fig. 175), μ_r'	0.63	0.80
Viscosity, micropoises	144.8	186.
Viscosity, lb/(hr)(ft)	0.0346	0.045
Compressibility factor (Fig. 103)	0.975	1.0
Molecular weight	43.3	55.8
Density, lb per cu ft	1.02	0.905

PHYSICAL PROPERTIES OF MIXTURE (*Continued*)

	Entering	*Leaving*
Diffusion coefficients, Equation (50) (sq ft per hr)		
D_{AB} (propylene–propane)	0.0392	0.0665
D_{AR} (propylene–polymer)	0.0247	0.0419
D_{Am} [Equation (17)]	0.0392	0.0618
Schmidt number, $\mu/\rho D_{Am}$	0.875	0.787
Reynolds number $D_p G/\mu$	147	113
j_d [Equation (46)]	0.142	0.163
$a_v H_{dG}$ [Equation (39)]	6.4	5.3

$$(H_{dG})_{\text{avg}},\ \text{ft} = (6.4 + 5.3)/(2)(144) = 0.0405$$

N_{dG} is evaluated from Equation (65):

$$\delta_A = (r - a)/a = (1 - 2.5)/2.5 = -0.6$$

At the entering conditions:

$$y_f = \frac{(1 + y_{Ai}\delta_A) - (1 + y_A\delta_A)}{\ln\left(\dfrac{1 + y_{Ai}\delta_A}{1 + y_A\delta_A}\right)} = \frac{1.0 - 0.772}{\ln\left(\dfrac{1.0}{0.772}\right)} = 0.881$$

For the low concentration of the outlet gas the arithmetic mean is satisfactory:

$$(y_f)_2 = (1.0 + 0.994)/2 = 0.997$$

$$(y_f)_{\text{avg}} = (0.881 + 0.997)/2 = 0.939$$

$$N_{dG} = 0.939 \ln\left[\frac{(0.38)(0.994)}{(0.01)(0.772)}\right] = 3.66$$

The thickness of the bed is obtained by Equation (59):

$$Z_2 - Z_1 = (3.66)(0.0405) = 0.148 \text{ ft or } 1.78 \text{ in.}$$

The hourly space velocity, based on total gas at 60°F and 30 in. Hg (saturated) is obtained by consideration of 1 sq ft of bed:

$$S_v = \frac{(200)(385.5)}{(43.3)(0.148)} = 12{,}000\ (1/\text{hr})$$

It is evident that a perfect catalyst under these conditions would result in very high reaction rates.

DIFFUSION IN POROUS CATALYSTS

In chemical reactions catalyzed by solid surfaces the reaction rate per unit mass of catalyst is influenced by the size and shape of the catalyst particle. In general an increase in gross external surface area or decrease in particle size for given surface conditions of temperature and component activities increases the rate. For a completely impervious catalyst the reaction is confined to the external surface, and the rate is hence directly proportional to the external surface area. In permeable catalysts the reaction extends to the interior surfaces, and the gross external area is generally a negligible fraction of the total effective interfacial area.

Commercial catalysts are manufactured in the forms of spheres, cylinders, irregular granules, and hollow cylinders. In the so-called fluid catalyst system the solid is suspended as a fine powder in a gas stream and thereby displays maximum exterior surface and effectiveness. In a stationary bed the pellets or granules are rarely used in sizes much less than $\frac{1}{8}$ in. in height and diameter because of excessive pressure drops, manufacturing difficulties, and the fact that further reduction in size frequently results in little gain in effectiveness.

The availability of the interior of the pellet for catalysis depends upon size, shape, and permeability of the pore structure. For high effectiveness it is required that the pores and capillaries be of large and reasonably uniform cross section and be interconnected with the external surface of the pellet. The effectiveness of the interior surface also depends upon the rate and nature of the reaction. A given pellet is relatively less effective for a gaseous reaction which proceeds at a high rate with an increase in number of gaseous moles than for one proceeding at a low rate with a decrease in moles and is also influenced by the effects of activated adsorption and the rapidity of the reverse reaction.

In considering the properties of a catalyst bed the external void space which surrounds the pellets should be distinguished from the internal voids within the particles. This distinction is established from the measurements of three densities, bulk density ρ_B expressed as mass per unit volume of bed; particle density ρ_p, mass per unit volume of particle: and solid density ρ_c, mass per unit volume of solid free from all voids, external and internal. For many catalysts the particle density is conveniently determined by displacement of mercury while the solid density is measured by helium displacement. The external void fraction of the bed is given by the relation,

$$F_e = 1 - \frac{\rho_B}{\rho_p} \tag{66}$$

and the internal void fraction by

$$F_i = 1 - \frac{\rho_p}{\rho_c} \tag{67}$$

It is evident that in a fluid reaction catalyzed by a porous solid the concentration of the fluid reactant at the interface will be lower at the interior surfaces than at the gross surface of the particle and that the rate of reaction per unit interfacial area will be lower at the interior surface. The ratio of the actual rate of reaction per unit mass of solid to the rate which would exist if the concentrations at all interior interfaces were the same as those at the gross exterior interface has been termed[5] the *effective-*

ness factor of the particle. A general equation for the rate of a reaction catalyzed by a porous solid may be written in the following form,

$$r_A = C\Delta a_i = E_A J \Delta a_i \tag{68}$$

where

r_A = reaction rate per unit mass
C = observed over-all rate factor of the reaction
Δa_i = driving force of the reaction in terms of activities at the external surfaces of the particle
E_A = effectiveness factor
J = the rate factor of the catalytic reaction which when multiplied by the driving force Δa_i gives the rate of reaction per unit mass of catalyst if the driving force is uniform throughout

For example, in Equation (XIX-36) the driving force, Δa_i is equal to $(a_{Ai} - a_{Ri}/K)$ while the rate factor J is equal to $(kLK_A)/(1 + a_{Ai}K_A + a_{Ri}K_R + a_{Ii}K_I + \cdots)$. For other mechanisms corresponding values for Δa_i and J can be obtained directly from the rate equations developed previously.

With an effectiveness factor of 1.0 the reaction rate at all interior surfaces is the same as that at the exterior surfaces. It is evident that this situation is approached when (1) the particle size is small, (2) the pores are large and well interconnected, (3) the rate factor of the reaction is relatively low, (4) the diffusion coefficients of reactants and products are high. The relations among these factors were developed by Thiele[14] by analyses of several simple cases which with the aid of reasonable simplifying assumptions could be treated mathematically. Thiele found that in the cases studied for a first-order reaction in which the rate is proportional to the first power of the concentration at the interface the effectiveness factor is a function of a modulus which is defined as follows:

$$E_A = f(m_T) = f\left[\frac{D'_p}{2}\sqrt{\frac{k}{cD_v}}\right] \tag{69}$$

where

$$m_T = \text{Thiele modulus} = \frac{D'_p}{2}\sqrt{\frac{k}{cD_v}}$$

D'_p = effective particle diameter for Thiele modulus
c = average radius of pores in the particle
D_v = diffusion coefficient
k = reaction velocity constant

---

[14] E. W. Thiele, *Ind. Eng. Chem.*, **31**, 916 (1939).

Rigorous expansions of this equation involving complex rate equations are difficult to develop and cumbersome to use.

It is evident from Equation (69) that Thiele's modulus is dependent upon the diffusional and reaction characteristics of the system, the structure of the solid, and the particle size. Both the reaction velocity constant and D_v are functions of temperature. The effective pore radius c is difficult to evaluate but for particles formed by the pelleting or extrusion of a given catalyst should be approximately proportional to the square root of the fraction of internal void volume. On this basis the modulus may be expressed in the following empirical form,

$$m_T = \frac{D'_p a' e^{b'/T}}{(F_i)^{\frac{1}{4}}} \tag{70}$$

where a' and b' are empirical constants, characteristic of the system

F_i = fraction internal voids from Equation (67)

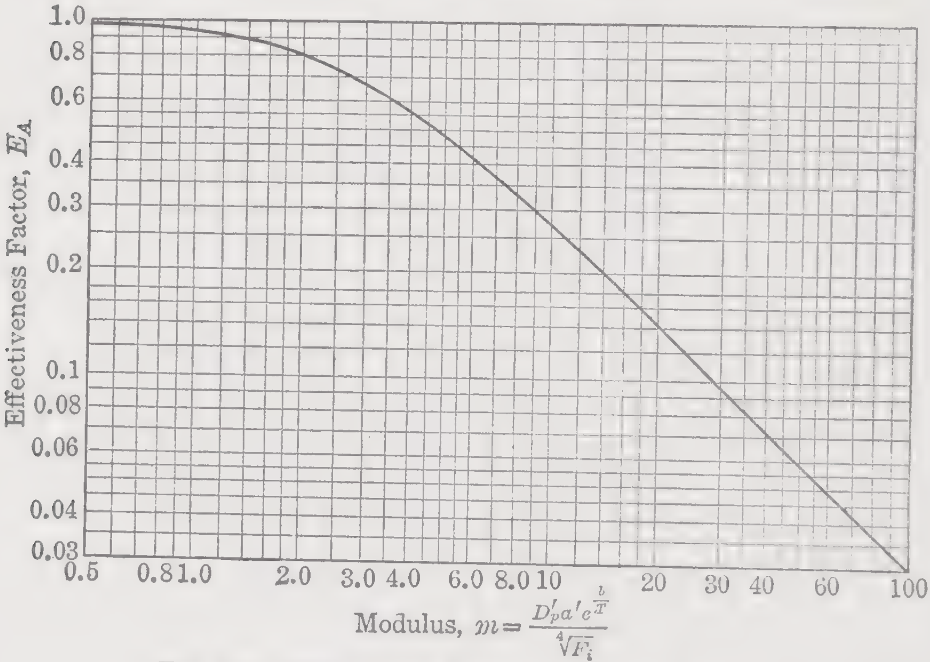

FIG. 195. Effectiveness Factor for Catalyst Pellets.
(Reproduced in "C.P.P. Charts")

Thiele found that for the several simple cases studied the effectiveness factor is related to the modulus by curves which do not differ greatly in general form. As an empirical approximation it was suggested that the curve derived by Thiele for spherical particles be assumed applicable in all cases and that D'_p be taken as the diameter of a sphere having the same surface area per unit volume as the particle in question. This curve is plotted in Fig. 195. It will be noted that at low values of the modulus the effectiveness factor approaches 1.0 indicating that the entire internal surface is reacting at a uniform rate. At high values of the modulus the effectiveness factor approaches inverse proportionality to the first power of the modulus. In this range the internal area is ineffective, and the reaction occurs only on the gross exterior surface of the particle. At low values of the modulus the reaction rate per unit mass of solid is independent of particle size, whereas in the high modulus range the rate is inversely proportional to the particle diameter.

The effective particle size D'_p for the Thiele modulus must be clearly distinguished from the effective particle size D_p used for mass-transfer correlations and defined by Equation (41). By definition,

$$D'_p = \frac{6V_p}{a_p} = \frac{6(1 - F_e)}{a_v} = \frac{6}{a_m \rho_p} \tag{71}$$

where V_p = average volume per particle
a_p = average gross exterior area per particle
F_e = fraction external void volume
a_v = surface area of particles per unit volume of bed
a_m = surface area per unit mass of particles
ρ_p = density of particles, mass per volume

For a cylinder whose diameter D is equal to its length, $D'_p = D$.

If Fig. 195 and Equation (70) are accepted for empirical application the constants of Equation (70) may be evaluated for a specific catalyst by comparing the reaction rates produced by two catalyst beds operated at identical conditions of temperature, pressure, and composition, but composed of particles having different known values of $D'_p/(F_i)^{\frac{1}{4}}$. The ratio of the two rates is equal to the ratio of the effectiveness factors, E_{A1}/E_{A2} of the two different pellets and the ratio of their moduli, m_{T1}/m_{T2}, is equal to $D'_{p1}(F_{i2})^{\frac{1}{4}}/D_{p2}(F_{i1})^{\frac{1}{4}}$. It is evident from inspection of Fig. 195 that evaluation of both E_{A1}/E_{A2} and the corresponding m_{T1}/m_{T2} serves to evaluate all four terms. On the logarithmic scales of this figure the ratio m_{T1}/m_{T2} corresponds to a fixed distance on the scale of abscissas, and the ratio E_{A1}/E_{A2} corresponds to a fixed distance on the ordinate scale. By constructing a right triangle whose base is equal to $\log (m_{T1}/m_{T2})$ and whose altitude is $\log E_{A1}/E_{A2}$ and moving the triangle along the curve with its hypothenuse as a chord, the properties of the two catalysts would correspond to the position at which the base of the triangle is parallel to the abscissa scale. This calculation is simplified by Fig. 196 which is derived from the mathematical equation of the curve of Fig. 195. This chart permits direct reading of m_{T1} from experimentally observed ratios of m_{T2}/m_{T1} and E_{A1}/E_{A2} at a constant temperature. In order to evaluate the constant b' of Equation (70) the entire procedure is repeated at another temperature.

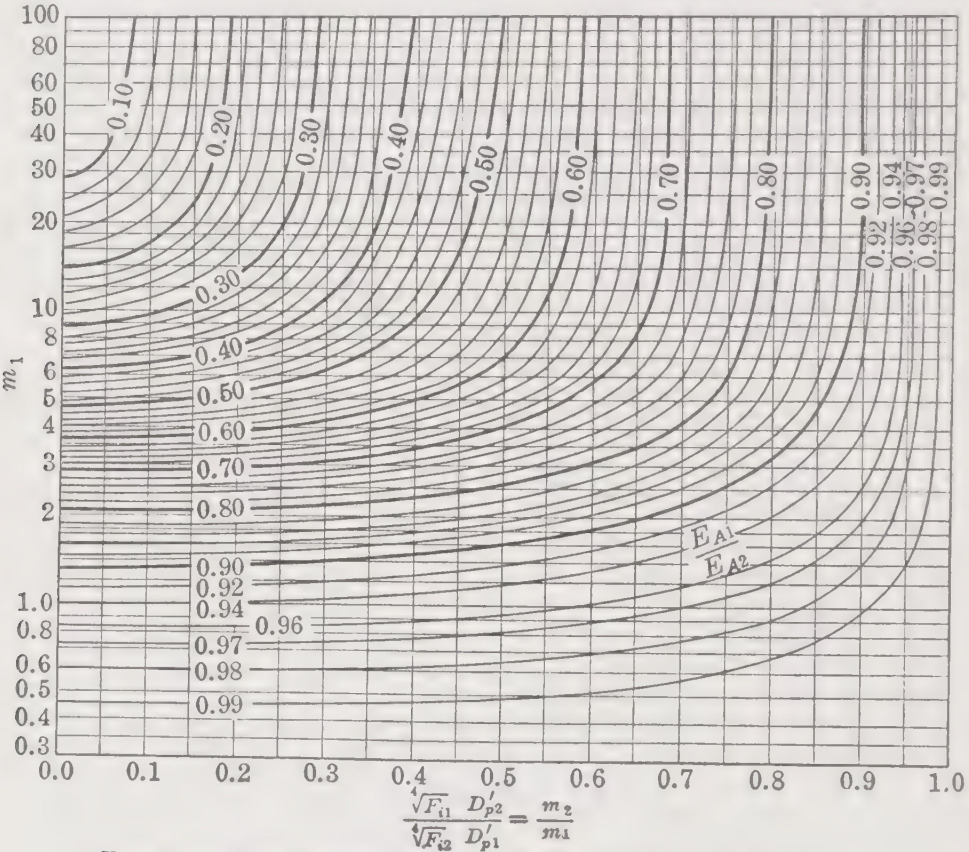

FIG. 196. Determination of the Effectiveness-Factor Modulus.
(Reproduced in "C.P.P. Charts")

Illustration 4. In order to evaluate the effectiveness factor of a nickel hydrogenation catalyst in the operation discussed in Illustration XIX-2 the following data were taken in a differential reactor. At each temperature the average activities of the reactants and products were adjusted to identical values for the two runs on the different catalysts.

Catalyst Size No.	1	2
Pellet diameter, D'_p, ft	0.0304	0.00425
Pellet density, ρ_p, lb per cu ft	123	124
Solid density, ρ_c, lb per cu ft	231	231
Temperature, °C	200	
r, lb-moles/(lb)(hr)	0.0364	0.0710
Temperature, °C	250	
r, lb-moles/(lb)(hr)	0.0458	0.0755

(*a*) Calculate the effectiveness factor and modulus of each catalyst size at the two temperatures.

(*b*) Evaluate the constants of Equation (70) for this catalyst.

(*c*) Calculate the effectiveness factor of this catalyst in the form of ½″ × ½″ cylinders with 40 per cent internal voids at a temperature of 275°C.

Solution:

Catalyst Size No.	1	2
Pellet area, sq in.	0.1338	0.00820
Pellet, volume, cu in.	0.00811	0.000695
D'_p, Equation (71), ft	0.0304	0.00425
F_i, Equation (67)	0.466	0.463
$(F_i)^{\frac{1}{4}}$	0.826	0.825
$D'_p/(F_i)^{\frac{1}{4}}$	0.0368	0.00514
Temperature, °C	200	250
$E_{A1}/E_{A2} = r_1/r_2$	0.513	0.606
$m_{T2}/m_{T1} = \dfrac{(D'_{p2})(F_{i1})^{\frac{1}{4}}}{(D'_{p1})(F_{i2})^{\frac{1}{4}}} =$	0.139	0.139
m_{T1} (Fig. 196)	4.8	3.7
m_{T2}	0.669	0.515
E_{A1} (Fig. 195)	0.50	0.60
E_{A2} (Fig. 195)	0.96	0.98

(*b*) Substituting in Equation (70) for catalyst size 1 gives

$$\log 4.8 = \log a' + \log 0.0368 + \frac{b'}{(2.303)(473)}$$

$$\log 3.7 = \log a' + \log 0.0368 + \frac{b'}{(2.303)(523)}$$

or

$$a' = 8.57; \qquad b' = 1290$$

(*c*) For ½″ × ½″ cylinders:

$$D'_p = \frac{0.5}{12} = 0.0418 \text{ ft} \qquad \frac{D'_p}{\sqrt[4]{F_i}} = \frac{0.0418}{\sqrt[4]{0.40}} = 0.053$$

$$F_i = 0.40$$

$$m_T, \text{ Equation (70)} = 8.57(0.053)e^{\frac{1290}{548}} = 4.71$$

$$E_A, \text{ Fig. 195,} = 0.50$$

It is frequently experimentally difficult to duplicate exactly the conditions of operation in a differential reactor when making comparisons of two different catalyst sizes by the procedure outlined in Illustration 4. Close duplication is desirable because of the irregularities generally encountered in kinetic relationships, but the effects of small variations in compositions or activities may be eliminated if a rate equation is available which is applicable to one size of catalyst. Thus, from Equation (68), where variations in J are negligible,

$$\frac{E_{A1}}{E_{A2}} = \frac{r_1(\Delta a_i)_2}{r_2(\Delta a_i)_1} \qquad (72)$$

In evaluating effectiveness factors from integral conversion data it is necessary to evaluate the space velocities which will result in the same conversion with different catalyst sizes when operated at the same feed composition, temperature, and pressure. The ratios of these space velocities at a constant conversion are then the ratios of the corresponding effectiveness factors. It is generally necessary to operate each catalyst size at two or more space velocities and determine the space velocity required for a given conversion by graphical interpolation.

It should be recognized that the effectiveness-factor relationship expressed by Fig. 195 is based on the assumption that the reaction approximates pseudo-first-order behavior over the limited range of conditions under consideration. This approximation may be far from correct where strong adsorption effects result in rates which pass through maxima with increases in partial pressures or temperatures. In such cases extrapolation of effectiveness-factor results is dangerous except for systems whose composition, pressure, or temperature are reasonably close to the range at which the empirical evaluation of the effectiveness factor was carried out. It is to be hoped that a more rigorous method of handling this problem may be developed.

Where consideration is restricted to a single type of catalyst of fixed particle size and density the effectiveness factor may be entirely ignored in developing rate equations. In such cases the variation of the effectiveness factor with temperature is included in the over-all rate constant C. However, an effectiveness factor far from unity tends to confuse the significance of the empirically determined effective adsorption-equilibrium constants in the rate equation and may result in poor agreement between observed rates and the simple forms of rate equations.

LONGITUDINAL DIFFUSION

In all of the developments of Chapters XIX and XX for flow reactors it is assumed that the longitudinal diffusion of reactants and products in the direction of flow is negligible. Diffusion of this type results from the concentration gradients established by the conversion of the reactants. Thus, products tend to diffuse back against the stream while reactants tend to diffuse forward. The relative importance of these effects depends on the magnitudes of the concentration gradients which in turn are determined by the depth of the catalyst bed and by the velocity of the fluid stream. In a reactor operated at a fixed space velocity the effects of longitudinal diffusion are negligible with a deep catalyst bed having a small cross-sectional area, but they may be of considerable importance in a shallow bed of large cross section. The situation is similar to that discussed in Chapter XVIII, page 865, for homogeneous reactions except that in fixed catalyst beds there is not the opportunity for convective circulation and large-scale eddy currents that exist in a vessel with no obstructions.

In the absence of convective circulation in the stream it may be considered that in a fixed catalyst bed operating adiabatically the net flow of all components at all points occurs in the direction of the main flow after steady-state conditions are reached. Thus, although a product may tend to flow back against the stream, no such flow actually occurs with respect to a fixed point in space under steady conditions of operation. The distribution of reactants and products must be such that the resulting concentration gradients will conform to the requirement of a uniform flow in one direction and at the same time satisfy Equation (1) for the diffusion of reactants and products relative to each other.

The mathematical requirements to be satisfied by the steady-state concentration gradients may be established by consideration of a downflow reactor and unit cross-sectional area to which the mass feed rate is F. At any cross-sectional plane at a distance Z from the inlet the net downward rate of mass flow must also equal F since there is no accumulation in the reactor. The net rate of flow of any individual reactant or product at position Z is then equal to the rate at which this material enters with the original feed plus the rate at which it is produced in the reactor section from the inlet to Z. Considering the reactant A, this net rate of flow past position Z is the sum of the rate at which A is carried downward by the movement of the stream and the rate at which it tends to diffuse downward in accordance with Equation (1) or (20). Thus, the net downward flow of A at position Z is equal to

$$Fn_A - \frac{D_{Am}\pi^2}{RT(\pi + p_A\delta_A)n_t}\frac{dn_A}{dZ} = Fn_{A_0} - \int_0^{Z_1} r_A\rho_B\,dZ \qquad (73)$$

where

F = feed rate, mass per unit time, per unit cross-sectional area
n_A, n_{A_0} = moles of A per unit mass of feed at section Z and at the inlet, respectively
n_t = total number of moles per unit mass of feed
D_{Am} = mean diffusion coefficient of A in the stream at position Z
$\delta_A = (r + s - a - b)/a$
r_A = rate of reaction of A, moles/(mass of catalyst)(time)
ρ_B = bulk density of catalyst bed

A second relationship may be established by means of a material balance for component A in an elementary volume dZ.

$$\text{Net flow of } A \text{ into element} \quad = Fn_A - \frac{D_{Am}\pi^2}{RT(\pi + p_A\delta_A)}\frac{dn_A}{n_t dZ} \tag{74}$$

Net flow of A out of element =

$$F(n_A + dn_A) - \frac{D_{Am}\pi^2}{RT(\pi + p_A\delta_A)n_t}\left(\frac{dn_A}{dZ} + \frac{d^2n_A}{dZ^2}\,dZ\right) \tag{75}$$

The difference between (74) and (75) is the rate of reaction of A in the element.

$$-Fdn_A + \frac{D_{Am}\pi^2}{RT(\pi + p_A\delta_A)n_t}\left(\frac{d^2n_A}{dZ^2}\right)dZ = r_A\rho_B dZ \tag{76}$$

Integration of Equation (76) is difficult because it is a second-order equation which requires two sets of boundary conditions to define a unique solution. These boundary conditions are fixed by the inlet and outlet conditions of the reactor at which discontinuities may be considered to exist both as regards reaction and diffusion. Progressive stepwise integration is not possible because conditions in even the first element of volume at the reactor inlet are dependent on the gradients throughout the entire bed. This becomes evident by consideration of the extreme case in which diffusion is so relatively rapid that the gradients throughout the bed are negligible except at the inlet. In this situation the conditions at the outlet may be assumed to prevail throughout the entire bed, as was done in Illustration 11 of Chapter XVIII, page 865.

The general problem of longitudinal diffusion has been analyzed by Hulburt[15] who developed integrated expressions for simplified cases. Even where these expressions are applicable their usefulness is limited by uncertainty as to the proper value of the diffusion coefficient. It is evident that the effective or apparent coefficient for diffusion in a stream flowing through a granular bed is quite different from that determined from static conditions in the absence of a granular solid.

In general, the mass velocities in commercial scale reactors with fixed catalyst beds are such that longitudinal diffusion is negligible. In the corresponding pilot-plant operations it may be a serious factor which should be carefully considered. Since the effects are difficult to analyze or to translate to large-scale operations it is desirable if possible to design the pilot plant so that they are negligible. This requires a catalyst bed sufficiently deep to minimize the gradients dn_A/dZ. Fortunately the problem is not serious in an experimental differential reactor in which only small incremental conversions are produced. Even though large concentration gradients are established in such a reactor their effect is

[15] H. M. Hulburt, *Ind. Eng. Chem.*, **36**, 1012 (1944); **37**, 1063 (1945).

small because the outlet composition differs but little from that at the inlet.

For a small experimental reactor of the integral type where large overall conversions are produced the design may be verified by applying Equation (73) to a small section at the inlet of the reactor.

$$-F\Delta n_A = r_A\rho_B\Delta Z - \frac{D_{Am}\pi^2}{RT(\pi + p_A\delta_A)n_t}\frac{\Delta n_A}{\Delta Z} \tag{77}$$

It is first assumed that diffusion is negligible, and Δn_A is calculated by omitting the last term of Equation (77). The last term is then evaluated with this value of Δn_A and the diffusion coefficient from Equations (17) and (50). If the last term is negligible in comparison with the second, longitudinal diffusion may be neglected. This calculation should be made for the reactant or product having the largest coefficient of diffusion.

Fluidized Catalyst Beds. In the so-called " fluid " catalytic process[16] the catalyst is carried upward as a fine powder into a large reactor vessel where a relatively dense fluidized bed of catalyst and reactants is maintained in a state of turbulence. Because of the limited velocity of flow which is permissible without excessive carry-over of catalyst the reactor beds are generally relatively short in comparison to their diameters. As a result of the turbulence inherent to the fluidized bed and this low ratio of length to diameter it is probable that the composition throughout the bed is approximately uniform, corresponding to the outlet conditions. This situation is comparable to that which would exist in a fixed bed operating at an extremely low mass velocity.

It is evident from the results of Illustration 11 of Chapter XVIII that this longitudinal mixing is undesirable in that a larger reactor or catalyst bed is required for a given conversion. A still more serious disadvantage is that longitudinal mixing may greatly increase the extent of secondary reactions because of the fact that the high concentration of products which exists at the outlet also prevails throughout the entire bed. As a result it would be expected that a fluidized catalyst bed will generally produce a lower conversion and a poorer selectivity than a fixed bed operated with the same weight of catalyst in the reactor per unit feed rate. This disadvantage may be in part offset by the higher effectiveness factor of the finely divided catalyst. However, the fluidized bed has the further disadvantage of a larger fraction of void volume which increases the extent of uncatalyzed side reactions in the homogeneous phase.

[16] E. V. Murphee, C. L. Brown, E. J. Gohr, E. C. Jahnig, H. Z. Martin, C. W. Tyson, *Trans. Am. Inst. Chem. Engrs.*, **41**, 19 (1945).

The ease of regeneration of a fluidized catalyst outweighs the inherent disadvantages of the fluidized bed where catalyst fouling is an important factor, and the longitudinal mixing in the bed may be minimized by various baffling arrangements which are undergoing considerable current development. Slowly moving catalyst beds of the TCC type[17] have flow and diffusional characteristics similar to those of fixed beds.

If the rate equations for all of the reactions involved are known the results of an unbaffled fluidized bed may be compared with those of a fixed bed by first calculating the conversion and selectivity corresponding to the operation of the fixed bed at a given space velocity. The product distribution obtained in this calculation is used as a basis for a first approximation to the product distribution from the fluidized bed. The space velocity of the fluidized operation and a corrected product distribution are then calculated by assuming that the outlet conditions prevail throughout the bed. On this basis the rate of each reaction per unit mass of catalyst may be directly calculated. The procedure is repeated until agreement is obtained between the assumed and calculated product distributions.

PROBLEMS

1. Estimate the diffusion coefficients of the following pairs of gases at 500°C and atmospheric pressure:

(*a*) CO_2—CO; (*b*) CO_2—O_2; (*c*) CO_2—N_2

(*d*) Estimate the diffusion coefficient of CO_2 in a gas mixture containing 15 per cent CO_2, 1 per cent CO, 80 per cent N_2, and 4 per cent O_2, at 500°C and atmospheric pressure.

2. Estimate the diffusion coefficients of *n*-butane, *n*-butene, and hydrogen in a stream of *n*-butane, 10 per cent of which has been dehydrogenated to *n*-butene and hydrogen at a temperature of 1075°F and a gauge pressure of 10 lb per sq in.

3. Estimate the value of p_f for the following reactions under the specified conditions:

(*a*) For the transfer of CO_2 in the reaction of CO_2 with carbon at atmospheric pressure with a main fluid composition of 15.3 per cent CO_2, 7.7 per cent CO, and 77 per cent N_2, where the partial pressure of CO_2 at the interface is zero.

(*b*) The same as (*a*) for a composition 1.7 per cent CO_2, 30.5 per cent CO, and 67.8 per cent N_2.

(*c*) The same over a reactor where terminal conditions correspond to (*a*) and (*b*)

(*d*) In the adiabatic evaporation of water in a stream of air at atmospheric pressure, 100°F and 50 per cent humidity.

4. A bed of cylindrical clay pellets having 39 per cent void volume is dried by through circulation of air. The surface area of the pellets per cu ft is 82.8 sq ft, and their equivalent diameter is 0.0542 ft. The air enters the bed at 0.985 atm, 160°F, wet bulb, 115°F, and a mass velocity of 1720 lb/(sq ft)(hr).

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[17] R. H. Newton, G. S. Dunham, and T. P. Simpson, *Trans. Am. Inst. Chem. Engrs.*, **41**, 215 (1945).

Calculate the rate of drying at the inlet conditions expressed in lb/(hr)(cu ft) of bed during the so-called "constant-rate" period when the particles may be considered as coated with liquid water.

5. Ammonia is produced at a rateof 7240 g per liter of catalyst per hour at 300 atm, and 380°C, in a 1:3 molal mixture of N_2 and H_2 entering a bed of a granular iron catalyst. The gas flows through the catalyst at a rate of 600 lb/(sq ft) (hr). The effective particle diameter D_p is 0.028 ft and the external surface area of the particles is 145 sq ft per cu ft. Estimate the temperature and partial pressure of nitrogen at the surface of the catalyst.

6. Normal butane is dehydrogenated by passing it through a catalyst bed contained in vertical tubes 2.5 in. in internal diameter and 12 ft long. The depth of the catalyst bed is 11 ft. The catalyst particles are $\frac{1}{8}'' \times \frac{1}{8}''$ cylinders arranged with 38 per cent void volume in the bed which has a bulk density of 52 lb per cu ft. The gaseous hourly space velocity is 1400 at standard conditions of 60°F and 29.5 in. Hg. Neglecting the effect of secondary reactions and pyrolytic side reactions and assuming the applicability of Equations (XIX-94–98), calculate the partial pressures and temperature of the butane, butenes, and hydrogen at the surface of the catalyst pellets at the point in the reactor where a conversion of 10 per cent is produced at a gas temperature of 1075°F and a gauge pressure of 10 lb per sq in. The results of problem 2 are applicable to this problem.

Estimate the percentage error resulting from neglect of heat- and mass-transfer effects under these conditions.

7. In the dryer described in problem 4 it is desired that the air shall leave the bed during the constant rate period with a percentage saturation of 90 per cent. Assuming that steady-state conditions are maintained and neglecting the heat capacity of the bed and the pressure drop through it, calculate:

(*a*) The temperature of the air leaving the bed.

(*b*) The height of a transfer unit at the average conditions of the bed.

(*c*) The number of transfer units required for the specified vaporization of water.

(*d*) The depth of the bed.

8. The bulk density of ρ_B of a catalyst bed, determined by direct weighing is 0.64 g per cc. The density of the bed with the external void spaces filled with mercury is 5.46 g per cc. When the catalyst bed is evacuated and filled with helium it is found that 0.756 milliliter of the gas is required per cc of bed at a pressure of 1.0 atm and a temperature of 74°F. Calculate:

(*a*) The fraction external voids.

(*b*) The pellet density ρ_p.

(*c*) The true density of the catalytic solid ρ_c.

(*d*) The fraction of internal void volume.

9. Butane is dehydrogenated at a high space velocity in a short catalyst bed to determine the effectiveness factor of the catalyst. The rates of reaction in the experimental reactor with a constant mass of catalyst were as follows with different sizes of catalyst in the form of cylinders whose heights and diameters are equal:

		$\longleftarrow r_A \longrightarrow$	
Diameter, in.	*Internal Void Fraction F_i*	*At* 1050°F	*At* 1100°F
0.125	0.51	2.68	5.52
0.250	0.40	1.90	3.41

(*a*) Calculate the apparent modulus and effectiveness factor of each catalyst size at each temperature.

(*b*) Estimate the effectiveness factor of a catalyst having a diameter of 0.080 in. and 36 per cent internal voids at a temperature of 1100°F.

10. An experimental reactor for the hydrogenation of butene codimer is operated isothermally at a temperature of 300°F, a pressure of 100 lb per sq in. and a liquid hourly space velocity of 0.5 at 60°F. The feed is pure codimer with hydrogen in 10 per cent excess of that required for complete saturation. The depth of the catalyst bed is 14 in. From Equation (77) estimate the relative importance of longitudinal diffusion in this reactor.

11. Normal butane is dehydrogenated in a catalyst bed having the properties of that described in problem 6. The operation is substantially isothermal at a temperature of 1060°F and a pressure of 1.0 atm. Integration of Equations (XIX-94–100) for these conditions as shown in Figs. 192 and 193 indicates that with an hourly W/F of 30 a conversion of 39 per cent and a selectivity of 89 per cent is obtained. The moles of products per mole of butane charged are as follows: Butenes, 0.346; hydrogen 0.39; dealkylation products, 0.09.

Assuming that the operation is carried out at the same temperature and pressure in a fluidized bed of the same catalyst in which the same fraction of void volume is maintained, calculate the W/F ratio and the product distribution corresponding to 39 per cent conversion, if Equations (XIX-94–100) are applicable.

(Actually the fraction of void volume in the fluidized bed would be considerably greater than in the fixed bed. However, Equations (XIX-94–100) do not properly separate uncatalyzed from catalyzed reactions and for this reason are restricted to a substantially constant fraction of void volume.)

CHAPTER XXI

CATALYTIC REACTOR DESIGN

The ultimate objective in the process design of a catalytic reactor is to arrive at the arrangement which will result in the most economical construction and operation. In general, the economic considerations are most complex and involve careful balancing of the yields and product distribution of the process against the capital costs of the plant and the operating costs represented by labor, utilities, and maintenance requirements. However, in any event, the first requisite for the intelligent selection of a plant design is the ability to predict the results which will be obtained with any specific arrangement proposed for study. These predictions must be based on the best possible interpretation of laboratory, pilot-plant, and any available commercial-scale data. In general, these data are best correlated as semiempirical rate equations and effective transfer coefficients, as discussed in the preceding sections. It is seldom practicable or possible to develop complete kinetic data prior to the design of a plant, and the engineer is forced to improvise and extrapolate fragmentary data to conditions far outside the range of his past experience. It is in such cases that sound fundamental principles are of the greatest value in breaking down the available information into component effects and contributions of such simplicity that their individual trends can be estimated with fair assurance.

After working correlations between operating conditions and results are established thedesign of the plant resolves itself intoa series of systematically planned " case studies." A set of operating and design conditions which appears attractive is selected, and the complete results of the proposed operation are calculated in order to establish the ultimate cost of the desired product. This procedure is then repeated for another case in which operating conditions or design factors are varied in the direction expected to reduce costs. The optimum design leading to the lowest costs is arrived at by consideration of the results of the entire series of cases. It is within the scope of this treatment to consider only the problem of predicting the conversions, product distributions, and complete operating conditions resulting from any primary reactor specifications which are selected for study.

GENERAL STEPWISE PROCEDURE

The fundamental catalytic rate equations developed in pages 910 to 926 are all in terms of the activities at the catalytic surface. In the case of a gaseous system in which the components form ideal solutions, the surface activity of a reactant is related to that in the fluid stream by the following expression:

$$a_{Ai} = a_A + \nu_A \,\Delta p_A \tag{1}$$

where a_{Ai} = activity of A at the surface of the catalyst pellet
a_A = activity of A in the fluid stream
$\Delta p_A = p_{Ai} - p_A$ = partial pressure difference required for the diffusion of A to the catalyst pellet, when ideal-gas behavior is assumed
ν_A = fugacity coefficient of A at the temperature and pressure of the system

Although there has been little investigation of diffusion of gases under nonideal conditions, it appears that the activity or fugacity gradient should be the correct driving-force term. Equation (1) is based on the assumption that with activities as driving forces diffusional data for ideal gases may be used where the ideal-gas law is not applicable. This assumption is in lieu of a more rigorous development for diffusion under nonideal conditions. The errors involved are rarely of any significance, and in most cases the fugacity coefficient is taken as 1.0.

In the case where mass transfer and chemical rates are both of importance, the rate of the general catalytic reaction $aA + bB \rightleftarrows rR + sS$ must be determined by successive approximations. A rate is assumed as a first approximation, frequently based on the assumption that mass transfer is negligible. On the basis of this rate the partial pressure difference between the fluid stream and the interface is calculated for each component by means of Equation (XX-48). Similarly, the temperature difference between the stream and the catalyst particles $(t_i - t) = \Delta t$ may be calculated from Equation (XX-49). The relationship between Δt and Δp_A is obtained by combining (XX-48 and 49)

$$\Delta t = \left(\frac{\Delta H_A \Delta p_A}{C_p p_f M_m}\right)\left(\frac{H_{hG}}{H_{dGA}}\right) = \left(\frac{j_d}{j_h}\right)\left(\frac{\Delta H_A \Delta p_A}{C_p p_f M_m}\right)\left(\frac{C_p\mu}{k}\right)_f^{\frac{2}{3}}\left(\frac{\mu}{\rho D_{Am}}\right)_f^{-\frac{2}{3}} \tag{2}$$

By means of Equations (XX-48 and 49) the temperature and the partial pressure of each component are calculated at the surface of the catalyst particle. A second approximation to the rate of reaction is then calculated on the basis of these pressures and temperature. The evaluation of the partial pressure and temperature differences is then repeated if necessary in order to establish an accurate rate.

It is theoretically necessary that the algebraic sum of the partial pressure differences of all components in a complex system shall be zero. Where an inert gas is present it may be considered that any unbalanced partial pressure difference between the reactants and products corresponds to a partial pressure difference of the inert component. Where an inert component is not present it may be necessary to adjust the partial pressures to an algebraic balance in order to compensate for inaccuracies in the approximate diffusional treatment which is used.

A complex problem in reactor design, involving simultaneous reactions, together with temperature and pressure variations may be worked out by combining this method for evaluating differential rates with the stepwise method of integration demonstrated in Illustration XVIII-13, page 875. Small sections of the reactor are considered successively and the conversion in each calculated on the basis of an average differential rate. Thus,

$$\Delta x_A = \frac{(r_A)_{\text{avg}}\,\Delta W}{F} \tag{3}$$

where

Δx_A = conversion of A moles per unit of initial feed
F = rate of feed per unit time
W = mass of catalyst
$(r_A)_{\text{avg}}$ = rate of conversion of A at the average conditions of the section

In each small section the partial pressure and temperature differences must be evaluated if they are of significance in determining the average rate. This operation is not difficult after the first two or three sections, because the partial pressure and temperature differences are all proportional to the rate of reaction and may be estimated from a projected plot of reaction rate against W/F.

As a part of such a progressive stepwise integration changes in total pressure and temperature in an adiabatic reactor are readily calculated from each section as in Illustration XVIII-13. In this manner complete temperature and pressure distribution curves are obtained. The relationships necessary for calculating pressure drops in granular beds are presented on page 1015. The case of temperature gradients in a nonadiabatic reactor where transverse temperature differences exist is discussed on page 1033. In an adiabatic reactor the temperature change in the fluid stream is calculated from the heat of reaction by the following differential energy-balance equation

$$\frac{dt}{dZ} = -\frac{r_A \rho_B \Delta H_A}{G C_p} \tag{4}$$

where

Z = distance in the direction of flow
ΔH_A = heat of reaction per mole of A reacted
C_p = heat capacity of fluid stream per unit mass

DIRECT GRAPHICAL INTEGRATION

Where variations in total pressure are not important direct graphical integration of the rate equations may be employed for predicting the performance of either an adiabatic reactor or one in which temperature is controlled in some known relationship to conversion. This procedure is illustrated diagrammatically in Fig. 197 for an exothermic reaction of the general type $A + B \rightleftarrows R + S$ in an adiabatic reactor in which variations in total pressure are small.

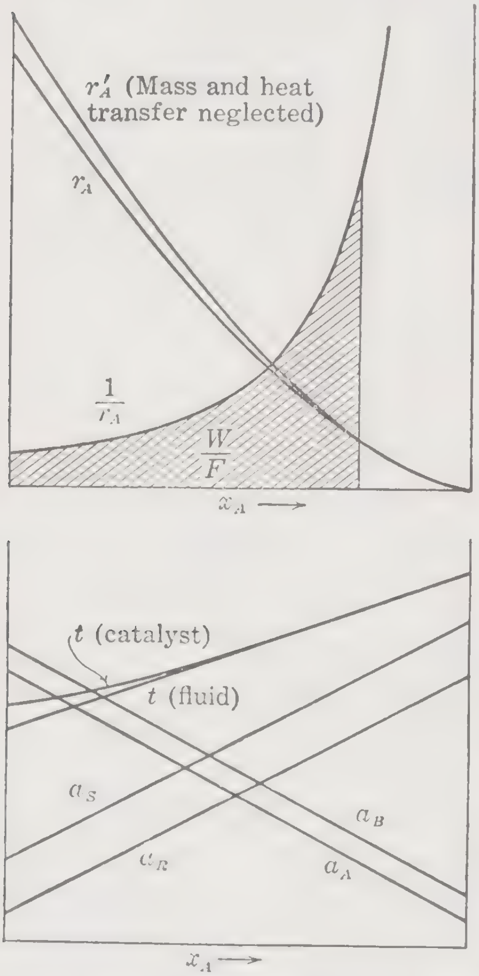

Fig. 197. Graphical Calculation of Reactor Size.

From the stoichiometry and thermochemistry of the reaction together with the specified initial conditions, the mole fractions, activities, and temperature of the reactants are plotted as functions of the conversion x_A. These relationships are plotted in the lower section of Fig. 197. From the activities and temperatures the corresponding rates of reaction r'_A are calculated, with mass and heat-transfer effects in the catalyst bed neglected. The corrected rate r_A and true catalyst temperature at the initial conditions are then calculated by the methods discussed in the preceding sections. If the effects of mass and heat transfer are not large the entire corrected rate curve may be approximated from this calculation at initial conditions by means of the following equation:

$$r_A = r'_A - (r'_{Ao} - r_{Ao}) \frac{r'_A(dr'_A/dx_A)}{r'_{Ao}(dr'_{Ao}/dx_{Ao})} \tag{5}$$

The ratio of derivatives in Equation (5) serves to improve the approximation where owing to adsorption effect the reaction rate is little influenced by conversion. If the mass transfer effects are large, trial-and-error corrections should be established at several conversions.

The mass of catalyst per unit feed rate which is required for a specified conversion x_A is obtained by determining the area under the curve relating $1/r_A$ to x_A, as indicated in the upper section of Fig. 197.

THE REACTOR UNIT CONCEPT

For simple reacting systems at constant temperature and pressure, analytical integration of Equation (XIX-64) may be expanded to include mass-transfer effects. In the case of a reaction which is unimolecular in both directions, represented by $A \rightleftarrows R$, there is frequently a range of conditions over which the effects of the adsorption terms in the denominator of Equation (XIX-36) are negligible and the rate equation may be written as

$$r_A = C\left(p_{Ai} - \frac{p_{Ri}}{K}\right) = C\left[p_A + \Delta p_A - \frac{(p_R + \Delta p_R)}{K}\right] \tag{6}$$

where Δp_A, Δp_R = differences between partial pressures of A and R, respectively, at the pellet surface and in the fluid stream. If the diffusional characteristics of the product and reactant are similar, as is generally the case in isomerization reactions of this type, it may be assumed that Δp_A and Δp_R are equal. Thus, from Equation (XX-48), if the mass transfer coefficient k_A is assumed to be the same for A and R, it follows that

$$\Delta p = \Delta p_A = -\Delta p_R = -\frac{r_A \rho_B}{k_A a_v} \tag{7}$$

Combining (6) and (7) gives

$$r_A = C\left(p_A - \frac{p_R}{K}\right) - \frac{C r_A \rho_B}{k_A a_v}\left(1 + \frac{1}{K}\right) \tag{8}$$

or, solving for r_A,

$$r_A = \frac{C(p_A - p_R/K)}{1 + \dfrac{C\rho_B}{k_A a_v}(1 + 1/K)} = \frac{C\pi\left(N_{Ao} - x_A - \dfrac{N_{Ro} + x_A}{K}\right)}{1 + \dfrac{C\rho_B}{k_A a_v}(1 + 1/K)} \tag{9}$$

Substituting (9) in (XIX-64) and integrating results in

$$\frac{W}{F} = \left(\frac{1}{C\pi} + \frac{\rho_B(1 + 1/K)}{k_A a_v \pi}\right) \int_{x_1}^{x_2} \frac{dx_A}{\left(N_{Ao} - \dfrac{N_{Ro}}{K}\right) - x_A\left(1 + \dfrac{1}{K}\right)} \tag{10}$$

or, if F is expressed in moles of feed per unit time, $F = SG/M_{mo}$

$$\frac{W}{\rho_B S} = Z = \left[\frac{G}{C\pi(1 + 1/K)M_{mo}\rho_B} + \frac{G}{M_{mo}k_A\pi a_v}\right] \ln\left[\frac{N_{Ao} - N_{Ro}/K - x_1(1 + 1/K)}{N_{Ao} - N_{Ro}/K - x_2(1 + 1/K)}\right] \tag{11}$$

where

Z = height of catalytic reactor
S = cross-sectional area of reactor
M_{mo} = mean molecular weight of the feed
ρ_B = bulk density of catalyst
G = mass velocity of feed

It may be noted that the second term in the brackets of Equation (11) is the height of a transfer unit for the mass transfer of A as defined by Equation (XX-37), neglecting changes in M_m. The other term in the brackets also has the dimension of length and is determined largely by the catalytic rate constant C, the mass velocity G, and the pressure π. A term of this general form has been designated by Hurt[1] as the *height of a catalytic unit* H_c, while the entire term in brackets is termed the *height of a reactor unit* H_R. Then by analogy to Equations (XX-58–59), the logarithmic term of Equation (11) represents the *number of reactor units* N_R required for the specified degree of conversion. Thus,

$$Z = (H_c + H_d)N_R = H_R N_R \tag{12}$$

where

H_c = height of a catalytic unit $= G/[C\pi(1 + 1/K)M_{mo}\rho_B]$
H_d = height of a transfer unit
N_R = number of reactor units $= (1 + 1/K) \displaystyle\int_{y_{A_2}}^{y_{A_1}} \frac{dy_A}{(y_A - y_A^*)}$
y_A = mole fraction of A in the gas stream
$y_A^* = y_R/K$ = the equilibrium value of y_A

Hurt pointed out the convenience of Equations (11) and (12) both for the correlation of rate data and the design of reactors under conditions of constant temperature and pressure. From measurements of conversion in a catalytic reactor to which these equations are applicable, the height of the catalytic unit H_c is readily calculated if Equations (XX-32–47) are used for the evaluation of H_d. The resultant values of $H_c\pi/G$ may be empirically plotted on a logarithmic scale against $1/T$, yielding an approximately straight line.

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[1] D. M. Hurt, *Ind. Eng. Chem.*, **35**, 522 (1943).

The development and application of Equations (6–12) are rigorous only for the assumed conditions of a reaction which is unimolecular in both directions and in a range of conditions in which the adsorption terms of the rate equation are negligible. The integrated equations are further restricted to conditions of constant temperature and pressure. Development of analogous treatments for more complex cases leads to cumbersome expressions.

Hurt showed that Equations (6–12) may be applied with fair accuracy to other than unimolecular reactions if all but one reactant are present in large excess, leading to a " pseudounimolecular behavior " at a constant total pressure. Where the adsorption of a product is important in retarding the rate of the reaction it was proposed that the height of the reactor unit be corrected by a " poisoning factor." Thus, for such a case where product R is strongly adsorbed and retards the reaction,

$$H_R = (1 + p_R k_R)(H_c + H_d) \tag{13}$$

where

k_R = " coefficient of poisoning " by product R
p_R = partial pressure of R

The coefficient k_R may be empirically correlated as a function of temperature.

It is evident that simplified treatments involving approximate linear relationships of this type may lead to large errors in some cases if they are applied to combinations of conditions not included in the range on which the empirical evaluations of the heights of the catalytic units and the coefficients are based. The assumptions involved are similar to those on which Figs. 190 and 191 are based. For this reason considerable discretion is necessary in their use. For general problems of reactor design which involve important variations in temperature and total pressure little saving in labor is effected as compared to more rigorous methods.

PRESSURE DROP IN GRANULAR BEDS

Extensive studies which have been carried out on the pressure drops of fluids flowing through conduits of uniform cross section are reviewed in detail in the standard texts on unit operations and hydraulics. These results are correlated by the dimensionless Fanning equation:

$$-\frac{dp}{dZ} = \frac{2fG^2}{g_c D \rho^2} \tag{14}$$

where

p = pressure in head of fluid
Z = length of path of flow
f = dimensionless friction factor
G = mass velocity per unit cross-sectional area
ρ = density, mass per unit volume
g_c = standard gravitational constant = 32.2 ft/(sec)^2
D = diameter for circular pipes = $4m_h$ for noncircular conduits
m_h = hydraulic radius = (cross-sectional area)/(perimeter)

The friction factor f is correlated as a function of the dimensionless Reynolds number N_{Re} which is defined as $4m_hG/\mu$ or for circular pipes DG/μ. The relationship between f and N_{Re} varies somewhat with the character of the surface but is approximately represented by the following equations[2] for flow in conduits:

$$N_{Re} < 2100; \qquad f = 16/N_{Re} \tag{15}$$

$$N_{Re} > 2100; \qquad f = 0.00307 + 0.189N_{Re}^{-0.38} \tag{16}$$

Equation (XVIII-98), page 869, is a modified form of the Fanning equation applicable in the region of Reynolds numbers above 100,000.

For flow through granular beds the Fanning equation may be modified to incorporate terms for the effective free cross-sectional area which is available for flow and the effective hydraulic radius of the path between the particles. This problem was studied by Oman and Watson[3] who pointed out the importance of the type of arrangement of the particles in the bed. If the bed is formed by adding particles at so slow a rate that each comes to rest before another falls on top of it, minimum bridging occurs and a high bulk density results. A bed formed in this manner is referred to as being in *random dense arrangement.* The opposite extreme termed *random loose arrangement* is obtained by simultaneously dumping all the particles of the bed into position. A stable arrangement results which shows no appreciable change in density with vibration. However, the bulk density may be as much as 20 per cent less than that of a random dense arrangement. It was found that the pressure drop through a dense bed may be nearly three times greater than through a loose bed of the same particles at the same superficial mass velocity of flow.

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[2] T. B. Drew, E. C. Koo, and W. H. McAdams, *Trans. Am. Inst. Chem. Engrs.*, **28**, 56 (1932).

[3] A. O. Oman and K. M. Watson, *Natl. Petroleum News*, Tech. Sec. **36**, *R*795 (November 1, 1944). Also "Process Engineering Data," National Petroleum Publishing Company, Cleveland (1944).

Either type of arrangement is fairly reproducible if care is used in forming the bed. A particularly undesirable type of bed which will produce nonuniform flow distribution or "channeling" results when both loose and dense arrangements are present in different sections. This situation can result if a large reactor is filled by dumping bags of pellets through a manhole and raking the bed level. Based on measurements of the pressure drop of air flowing through various types of granular packing materials and a review of the data of the literature, Oman and Watson proposed the following dimensionless equation for beds in random dense arrangement:

$$-\frac{dp_D}{dZ} = \frac{2f_D G^2 a_v}{\rho g_c F_D^{1.7}} \tag{17}$$

where

p_D = pressure in a bed in dense arrangement expressed in force (mass units) per unit area
Z = length of packed bed
f_D = friction factor for dense arrangement as a function of the modified Reynolds number $N_{Rep} = G/a_v\mu$
g_c = standard gravitational constant = 32.2 ft/(sec)^2
G = mass velocity per unit of total cross-sectional area of the bed
a_v = surface area of particles per unit volume of bed
F_D = fraction of void space in the bed in dense arrangement $= (1 - \rho_B/\rho_p)$
ρ = density of fluid
ρ_p = average density of solid particles
ρ_B = apparent bulk density of the granular bed

The recommended relationship between f_D and the modified Reynolds number N_{Rep} is approximately represented by the following two equations,

$$f_D = 2.60(N_{Rep})^{-0.3} \quad \text{[for values of } N_{Rep} \text{ from 10 to 150]} \tag{18}$$

$$f_D = 1.23(N_{Rep})^{-0.15} \quad \text{[for values of } N_{Rep} \text{ from 150 to 300]} \tag{19}$$

where $N_{Rep} = G/a_v\mu$

It may be noted that the modified Reynolds number used for pressure-drop calculations is quite different from that found best for heat- and mass-transfer correlations. This is due to the situation that in fluid flow, pressure drop is affected by the configuration of void spaces whereas the rates of mass and heat transfer are controlled principally by the superficial area of the particles.

Correlation of pressure drops in beds in loose arrangement was less satisfactory than for dense beds. For the general case Equation (17) is modified to include a factor which is a function of the difference between the fraction of voids in the bed under consideration and that in a bed of the same particles in random dense arrangement. Thus,

$$\frac{dp_L}{dZ} = \left(\frac{2f_D G^2 a_v}{\rho g_c F_L^{1.7}}\right)\left(\frac{f_L}{f_D}\right) \tag{20}$$

where

f_L = friction factor for the loose arrangement
F_L = fraction of voids in the loose arrangement
f_D = friction factor from Equations (18) and (19) corresponding to the N_{Rep} calculated from the value of a_v for the loose arrangement

The ratio f_L/f_D is expressed as an approximate function of $(F_L - F_D)$ by the following equation:

$$f_L/f_D = 1.0 - 3.5(F_L - F_D) \tag{21}$$

Equations (18–21) were found to be applicable with errors generally less than 20 per cent to a variety of shapes of particles including spheres, cylinders, rings, saddles, and crushed fragments. For irregular crushed fragments the surface area per unit volume a_v was calculated by the following expression which assumes a surface–volume relationship midway between that of a cube and a tetrahedron,

$$a_v = 6.6N^{\frac{1}{3}}(1 - F_e)^{\frac{2}{3}} \tag{22}$$

where

N = number of particles per unit volume
F_e = fraction of voids volume

Where the total pressure drop in a reactor is small in comparison to the total pressure, Equations (17) and (20) may be written in incremental form and Δp calculated directly from the average conditions. For larger pressure drops a graphical integration is desirable because of the variation of ρ with both pressure and molecular weight. Ordinarily it is satisfactory to use an average value of the friction factor. For ideal-gaseous systems ρ is given by the following expression

$$\rho = \frac{M_{mo}p}{(1 + \delta_A x_A)RT} \tag{23}$$

where

x_A = moles of A converted per mole of feed
δ_A = increase in number of moles per mole of A converted

Combining (23) with (17) and integrating gives

$$p_o^2 - p^2 = \frac{4f_D G^2 a_v R}{g_c F_D^{1.7} M_{mo}} \int_{Z_o}^{Z} (1 + \delta_A x_A) T \, dZ \tag{24}$$

Equation (24) frequently must be used by successive trials. A preliminary relationship of conversion, temperature, and bed depth is calculated as indicated in Fig. 197, an approximate pressure distribution being assumed. A corrected pressure distribution is then calculated by graphical integration of Equation (24). This revised pressure curve may then be used for an improved relationship between bed depth and conversion.

It is sometimes desired to carry out an operation to produce a specified conversion with a specified pressure drop through the reactor. If mass-transfer effects are not large an approximate space velocity for the required conversion may be obtained by an integration of the type of Fig. 197 with an assumed pressure distribution curve. It is then necessary to calculate the bed depth Z_1 which corresponds to the required space velocity and the specified pressure drop. The relation between mass velocity and space velocity is as follows

$$G = S_v \rho_f Z_1 \tag{25}$$

where ρ_f is the density of the feed at the standard conditions for the expression of space velocity.

Combination of Equations (23) and (25) with (17) and (18) and integration gives, for modified Reynolds numbers less than 150,

$$Z_1^{2.7} = \frac{0.193 g_c F_D^{1.7} M_{mo}}{(S_v \rho_f)^{1.7} a_v^{1.3} R \mu^{0.3}} \int_p^{p_o} \frac{p\,dp}{(1 + \delta_A x_A) T} \tag{26}$$

Equation (26) corresponds to a fixed space velocity with mass velocities varying in accordance with Equation (25). It is not applicable to calculations of the pressure drop distribution in a bed in which the mass velocity is constant. In the use of Equation (26) approximate relationships between p, x_A and T may be assumed for the first integration. An improved pressure distribution relationship may then be calculated by Equation (24) and used as a basis for a new relationship between bed depth and conversion by an integration of the type of Fig. 197. A few trials of this type will establish all factors within the accuracy ordinarily justified by the data.

Optimum Pressure Drop. The selection of an optimum pressure drop is generally a most complicated problem. As is pointed out in Chapter XX, it is desirable to operate at high mass velocities in order to minimize both the resistance to mass transfer to and from the catalyst particles and the undesirable effects of longitudinal diffusion. However high mass velocities result in high pressure drops which may be undesirable from three viewpoints:

1. A high pressure drop may increase the rates of undesirable reactions and reduce the selectivity corresponding to a given outlet pressure.
2. Excessive pressure drops may result in the crushing and disintegration of fragile catalysts.
3. Frequently a high pressure drop corresponds to a significant power cost for compression.

All of these factors must be considered in arriving at the mass velocity and pressure drop which result in the most economical over-all operation.

OPTIMUM REACTION TEMPERATURES

Since reaction velocity constants are always increased by increased temperature there are many cases in which reaction rates increase progressively with temperature and the maximum rate corresponds to the highest temperature attainable. In such cases the optimum temperature of operation is determined by such factors as the physical and mechanical properties of the catalyst and the materials of construction, the effect of temperature on undesirable side reactions, the problem of preheating to high temperatures without decomposition, and the problems of heat transfer which accompany high reaction rates.

Increased temperature may lead to diminished rates of reaction in two general cases. The first is encountered in both homogeneous and heterogeneous systems when an exothermic reaction approaches equilibrium conditions. Under these conditions, the decrease in the equilibrium constant with increased temperature may more than offset the increase in the reaction velocity constant so that a reduction in rate results. The other case, which is encountered in heterogeneous catalytic reactions, occurs when the adsorption-equilibrium constants are reduced by temperature at a greater rate than the reaction velocity constant is increased. For example, in Equation (XIX-42) the group of terms kK_AK_B may decrease with increased temperature, even though k itself always increases. In such a case the rate of reaction may increase at low temperatures but decrease at high temperatures where the adsorption terms in the denominator of the rate equation become small.

In all cases where reaction rates may be diminished by increased temperature, a well-defined optimum temperature exists which will result in a maximum rate of reaction at specified conditions of composition, pressure, and mass velocity. The minimum reactor size is obtained when the temperature is controlled at the optimum at all points. Since the optimum temperature generally varies as conversion proceeds, elaborate cooling or heating provisions may be required to approach this condition.

The optimum temperatures for a reaction at constant pressure and mass velocity may be determined by using the methods described in the preceding sections to calculate reaction rates at various temperatures and conversions. The resultant data may be plotted as lines of constant conversion or degree of completion with reaction rates as ordinates and temperatures as abscissas. Such a plot is shown in Fig. 198 for the catalytic oxidation of SO_2 in the system described in Illustrations XVI-6, 8, 12, and 13, pages 716, 720, 726, and 728. This chart is restricted to a pressure of 1.0 atm and a mass velocity of 600 lb/(hr)(sq ft). Similar charts for other conditions may be developed by the methods demonstrated in the following illustration.

Illustration 1. The kinetics of the oxidation of SO_2 on a platinum catalyst were reviewed by Uyehara and Watson[4] and Hurt.[1] The general rate equation proposed by Uyehara and Watson was subsequently modified to agree with the temperature effects indicated by the new data of Hurt. This modified equation is as follows:

$$r = \frac{e^{-\frac{8000}{T} + 14.154}}{(1 + \sqrt{p_{iO_2}K_{O_2}} + p_{iSO_3}K_{SO_3})^2}\left[p_{iSO_2}\sqrt{p_{iO_2}} - \frac{p_{iSO_3}}{K}\right]$$

where

r = reaction rate, lb-moles SO_2 oxidized/(hr)(lb catalyst)
T = degrees Kelvin at catalyst surface
p_{iSO_2} p_{iO_2}, p_{iSO_3} = the respective partial pressures of the active components *at the catalyst surface*, atmospheres

$$K_{O_2} = e^{\frac{20{,}360}{RT} - \frac{23.0}{R}}$$

$$K_{SO_3} = e^{\frac{16{,}800}{RT} - \frac{17.51}{R}}$$

K = the over-all gas-phase equilibrium constant (Fig. 156)

The gas mixture specified in Illustration XVI-6, page 716, enters the reaction at a temperature of 400°C, 1.0 atm, and a mass velocity of 600 lb/(hr)(sq ft). The catalyst is in the form of ⅜″ × ⅜″ cylindrical pellets of such porosity that it may be assumed that the effectiveness factor is 1.0 and that the foregoing rate equation is applicable. The bed is in random dense arrangement with a void fraction of 0.35

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[4] O. A. Uyehara and K. M. Watson, *Ind. Eng. Chem.*, **35**, 541 (1943).

and a bulk density of 50 lb per cu ft. At the conditions of the reactor inlet it is desired to calculate:

(*a*) The rate of conversion of SO_2 in lb-moles/(hr)(lb).

(*b*) The temperature of the catalyst pellets.

(*c*) The pressure drop per inch of bed depth.

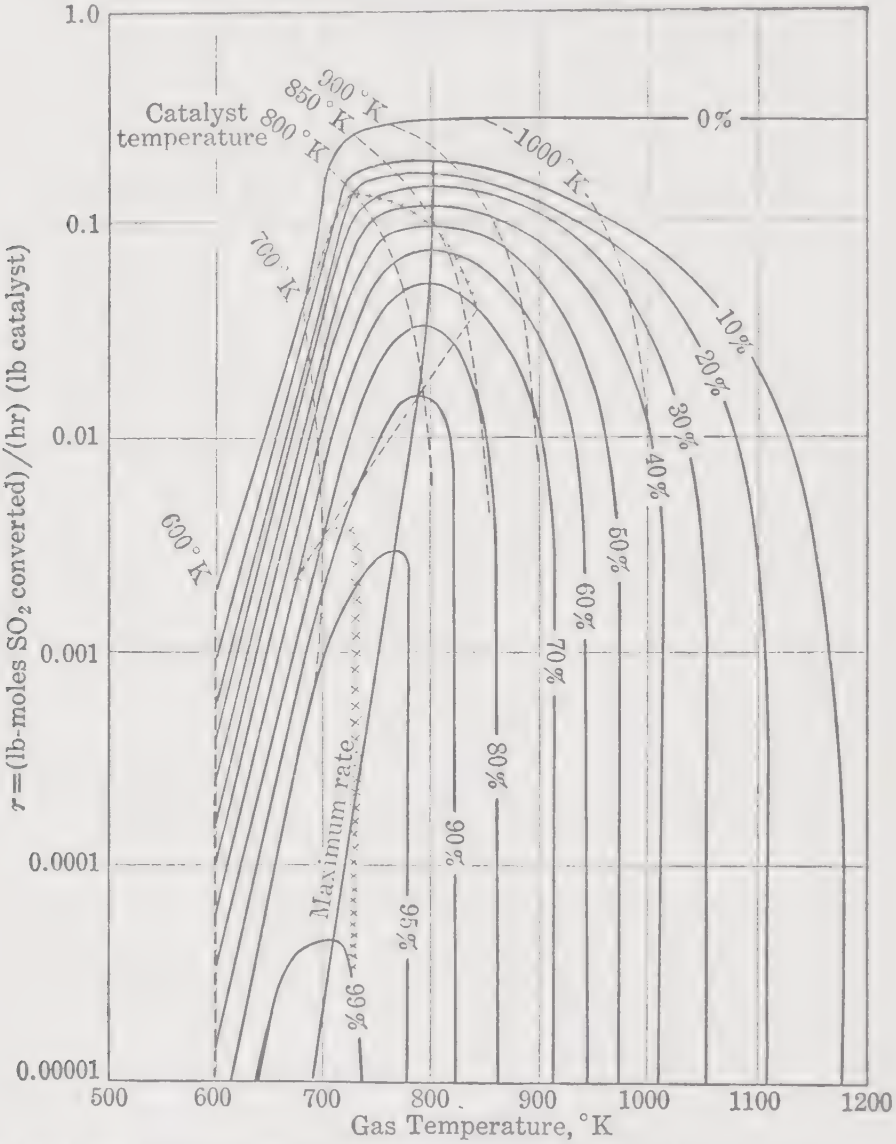


Fig. 198 Effect of Temperature and Conversion on the Rate of Catalytic Oxidation of Sulfur Dioxide. (Composition of Entering Gas, 7.8% SO_2, 10.8% O_2, 81.4% N_2). G = 600 lb/(hr)(sq ft)

(*d*) The rise in temperature of the gas stream/inch of bed depth at entrance conditions.

Solution: As a first approximation the rate of reaction is calculated with the assumption that the partial pressures and temperature at the interface are the same as those of the gas stream. At 400°C,

$$4.575 \log K_{O_2} = \frac{20{,}360}{673.1} - 23; \qquad K_{O_2} = 38.46; \qquad \sqrt{K_{O_2}} = 6.20$$

$$4.575 \log K_{SO_3} = \frac{16{,}800}{673.1} - 17.51; \qquad K_{SO_3} = 42.46$$

From Fig. 156, $K = 930$

$$2.3026 \log C = -\frac{8{,}000}{673.1} + 14.154; \qquad C = 9.663$$

$$r_m = \frac{9.663\left[(0.078)\sqrt{(0.108)} - \dfrac{0}{930}\right]}{[1 + 6.20\sqrt{0.108} + 42.46(0)]^2} = 0.0268$$

For calculating the partial pressure and temperature differences across the gas film the physical properties of the system must be evaluated. The properties of the pure components are summarized in Table A. The critical viscosity of SO_3 was calculated from Equation (XVIII-102).

TABLE A

Component	SO_2	O_2	SO_3	N_2
M	64	32	80	28
T_c, °K	430.3	154.3	491.4	126.0
p_c, atm	77.7	49.7	83.6	33.5
μ_c, micropoises	411	250	469	180

In order to be rigorously correct the viscosity of the mixture should correspond to the average conditions in the film for calculating the Schmidt number and the average conditions of the fluid stream for calculating the Reynolds number. However, the differences are ordinarily not large, and it is generally satisfactory to base the Schmidt number on the main stream conditions. On this basis:

$$M_m = (0.078)(64) + (0.108)(32) + (0.814)(28) = 31.23$$
$$T_c' = (0.078)(430.3) + (0.108)(154.3) + (0.814)(126) = 152.5$$
$$p_c' = (0.078)(77.7) + (0.108)(49.7) + (0.814)(33.5) = 38.64$$
$$\mu_c' = (0.078)(411) + (0.108)(250) + (0.814)(180) = 205.3$$

$$T_r' = 673.1/152.5 = 4.41; \quad p_r' = \frac{1.0}{38.64} = 0.0259$$

$$\mu_r' \text{ (Fig. 175)} = 1.51$$
$$\mu = (1.51)(205.3) = 310 \text{ micropoises} = (310)(0.000242) = 0.0746 \text{ lb/(ft)(hr)}$$
$$\rho = \frac{(31.23)(273.1)}{(359)(673.1)} = 0.0354 \text{ lb per cu ft}$$

The diffusivities of the individual pairs are calculated from Equation (XX-50). The molecular volume of SO_3 is estimated as 47.8.

$$D_{SO_3-O_2} = \frac{(0.0043)(673.1)^{\frac{3}{2}}}{[(47.8)^{\frac{1}{3}} + (25.6)^{\frac{1}{3}}]^2}\sqrt{\frac{1}{80} + \frac{1}{32}} = 0.366 \text{ sq cm per sec}$$

Similarly,

$$\begin{aligned} D_{SO_3-N_2} &= 0.362 \\ D_{SO_3-SO_2} &= 0.244 \\ D_{SO_2-O_2} &= 0.385 \\ D_{SO_2-N_2} &= 0.383 \\ D_{O_2-N_2} &= 0.525 \end{aligned}$$

The mean diffusivity of each diffusing component in the mixture is calculated from Equation (XX-17) and converted to square feet per hour by the factor 3.88.

$$D_{SO_3m} = (0.108)(0.366) + (0.814)(0.362) + (0.078)(0.244)$$
$$= 0.354 \text{ cm}^2/\text{sec or } 1.37 \text{ sq ft per hr}$$

$$D_{SO_2m} = \frac{(0.108)(0.385) + (0.814)(0.383)}{(1 - 0.078)} = 0.380 \text{ cm}^2/\text{sec or } 1.47 \text{ sq ft per hr}$$

$$D_{O_2m} = \frac{(0.078)(0.385) + (0.814)(0.525)}{(1 - 0.108)} = 0.511 \text{ cm}^2/\text{sec or } 1.98 \text{ sq ft per hr}$$

$$D_{N_2m} = \frac{(0.078)(0.383) + (0.108)(0.525)}{(1 - 0.814)} = 0.463 \text{ cm}^2/\text{sec or } 1.80 \text{ sq ft per hr}$$

The corresponding Schmidt numbers follow directly from the mean diffusivity of each component together with the average viscosity and density of the mixture. The effective diameter for the modified Reynolds number for mass and heat transfer is calculated from Equation (XX-42) and the transfer factors from Equations (XX-46–47).

$$D_p = (\tfrac{3}{8})\sqrt{1.5} = 0.458 \text{ in. or } 0.0383 \text{ ft}$$

$$\frac{D_pG}{\mu} = \frac{(0.0383)(600)}{0.0746} = 308; \qquad j_d = 1.82(308)^{-0.51} = 0.0984$$

$$j_h = 1.95(308)^{-0.51} = 0.1048$$

The average molal heat capacity of the gas is obtained from Table IV, page 212. Thus at 400°C,

$$c_p = (0.078)(12.03) + (0.108)(7.84) + (0.814)(7.31) = 7.74$$

or, on a pound basis,

$$C_p = \frac{7.74}{31.23} = 0.248$$

From Equation (XX-51),

$$\left(\frac{C_p\mu}{k}\right)^{\frac{2}{3}} = \left[\frac{4}{9 - 5\dfrac{(5.74)}{7.74}}\right]^{\frac{2}{3}} = 0.830$$

The value of $a_v H_{hG}$ is then calculated from Equation (XX-40):

$$a_v H_{hG} = \frac{1}{j_h}\left(\frac{C_p\mu}{k}\right)^{\frac{2}{3}} = \frac{0.830}{0.1048} = 7.92$$

The gross exterior catalyst surface per unit volume of bed is obtained from Equation (XX-43):

$$a_v = \frac{6(0.65)(12)}{\frac{3}{8}} = 125 \text{ sq ft per cu ft}$$

Then,
$$H_{hG} = \frac{7.92}{125} = 0.0632 \text{ ft}$$

The values of $a_v H_{dG}$ and H_{dG} for the diffusion of the individual components are calculated from Equations (XX-39) and summarized in Table B.

TABLE B

	$\frac{\mu}{\rho D_{Am}}$	$\left(\frac{\mu}{\rho D_{Am}}\right)^{\frac{2}{3}}$	$a_v H_{dG}$	H_{dG}
SO_3	1.54	1.334	13.50	0.1080
SO_2	1.435	1.272	12.90	0.103
O_2	1.062	1.041	10.50	0.084
N_2	1.19	1.116	11.30	0.0905

Since the mole fractions of all the diffusing components are small the values of p_f are satisfactorily approximated by the arithmetic mean rather than the logarithmic mean of Equation (XX-25). From the stoichiometry of the reaction,

$$\delta_{SO_2} = -0.5 \qquad \delta_{O_2} = -1.0 \qquad \delta_{SO_3} = -0.5$$

In the first approximation p_{fSO_3} may be taken as 1.0 and the factors for SO_2 and O_2 based on the main stream partial pressures. Thus

$$p_{fSO_2} = 1.0 - (0.5)(0.078) = 0.961 \text{ atm}$$
$$p_{fO_2} = 1.0 - (0.108) = 0.892 \text{ atm}$$

The partial pressure differences for each component may be calculated from Equation (XX-48) using the rate arrived at by neglect of diffusion. Thus, since $G/M_m = 600/31.23 = 19.18$,

$$\Delta p_{SO_3} = \frac{r\rho_B p_{fSO_3} H_{dSO_3} M_m}{G} = \frac{(0.0268)(50)(1.0)(0.1080)}{19.18} = 0.00756$$

$$\Delta p_{SO_2} = -\frac{r\rho_B p_{fSO_2} H_{dSO_2} M_m}{G} = -\frac{(0.0268)(50)(0.961)(0.103)}{19.18} = -0.00693$$

$$\Delta p_{O_2} = -\frac{r\rho_B p_{fO_2} H_{dO_2} M_m}{2G} = -\frac{(0.0268)(50)(0.892)(0.084)}{(2)(19.18)} = -0.00263$$

The first approximation partial pressures at the interface are then

$$p_{iSO_3} = 0 + \Delta p_{SO_3} = 0 + (0.0076) = 0.0076$$
$$p_{iSO_2} = 0.078 + \Delta p_{SO_2} = 0.078 - 0.0069 = 0.0711$$
$$p_{iO_2} = 0.108 + \Delta p_{O_2} = 0.108 - 0.0026 = 0.1054$$

An expression for the heat of reaction at any temperature is obtained by substituting the thermochemical data of Illustration XVI-12, page 726, in Equation (VIII-65), page 305.

At 673.1°K, $\Delta H_{SO_2} = -23{,}832$ cal per g-mole

Since the heat of reaction is liberated at the interface it is transferred to the gas stream as a result of a temperature difference which is expressed by Equation (2).

$$\Delta t = \frac{\Delta H_A \Delta p_A H_{hG}}{C_p M_m p_f H_{dG}} = \frac{(-23{,}832)(-0.00693)(0.0632)}{(0.248)(31.23)(0.961)(0.103)} = +13.6°\text{C}$$

The second approximation to the temperature of the catalyst is then 673.1 + 13.6 = 686.7°K. The constants of the rate equation at this temperature are

$$C = 12.13; \qquad \sqrt{K_{O_2}} = 5.35; \qquad K_{SO_3} = 33.19$$
$$K = 660; \qquad \Delta H_{SO_2} = -23{,}860; \qquad c_p = 7.76$$

A second approximation to the rate is calculated with these constants

$$r_{mSO_2} = 0.0312$$

Second-approximation partial pressure and temperature differences may be calculated from this corrected rate. Since the values of $a_v H_{dG}$ vary but little with changes in the temperature or composition of the system they need not be corrected. Corrected values of the film pressure factor are:

$$p_{fSO_3} = [1.0 + 1.0 + (0.5)(0.0076)](\tfrac{1}{2}) = 1.002$$
$$p_{fSO_2} = [1.0 - (0.5)(0.078) + 1.0 - (0.5)(0.0711)](\tfrac{1}{2}) = 0.963$$
$$p_{fO_2} = [1.0 - (1.0)(0.108) + 1.0 - (1.0)(0.1054)](\tfrac{1}{2}) = 0.893$$

Then

$$\Delta p_{SO_3} = 0.0088 \qquad p_{iSO_3} = 0.0088$$
$$\Delta p_{SO_2} = -0.0081 \qquad p_{iSO_2} = 0.0699$$
$$\Delta p_{O_2} = -0.0031 \qquad p_{iO_2} = 0.1049$$
$$\Delta t = 15.3 \qquad T_i = 688.4°\text{K}$$

A third-approximation rate calculated on the basis of these interface pressures and temperature is 0.0312 lb mole/(hr)(lb) which gives results in agreement with the second approximation.

The pressure drop per inch of bed depth is calculated from Equation (17).

$$\frac{G}{a_v\mu} = \frac{600}{(125)(0.0746)} = 64.3$$

From Equation (18),

$$f_D = 2.60(64.3)^{-0.3} = \frac{2.60}{3.48} = 0.745$$

$$-\frac{dp_D}{dZ} = \frac{2f_D G^2 a_v}{g_c \rho F_D^{1.7}} = \frac{2(0.745)(600)^2(125)}{(32.2)(0.0354)(0.35)^{1.7}(3600)^2} = 27.2 \text{ lb/(sq ft)(ft)}$$

or

$$\frac{27.2}{1728} = 0.0158 \text{ lb/(sq in.)(in.)}$$

The temperature rise at the inlet of the reactor is calculated from Equation (4):

$$\frac{dt}{dZ} = -\frac{r_A \Delta H_{A\rho B}}{GC_p} = \frac{-0.0312(-23{,}858)(50)}{(600)\dfrac{7.76}{31.23}(12)} = 20.8°\text{C per in.}$$

A rigorous procedure is followed in Illustration 1 to demonstrate the principles involved. In many cases much simplification is justified. If diffusional effects are not large and the reactants and products are of similar physical properties an average diffusivity and height of transfer unit may be used for all. If the equilibrium constant is large the diffusional gradients of the products may be neglected. In many cases variations in the film pressure factor p_f may be neglected, and in dilute systems it may be assumed to equal the total pressure.

The result of Illustration 1 represents one point on Fig. 198. Other points corresponding to other conditions of temperature and conversion may be calculated in the same manner. The effects of ignoring the diffusional and temperature difference corrections in such calculations are shown graphically in Fig. 199. The solid-line curves in this figure correspond to those of Fig. 198. The broken-line curves are the results obtained if the indicated corrections are neglected. It may be noted that the corrections are very important where the rates are high, but become insignificant at low rates.

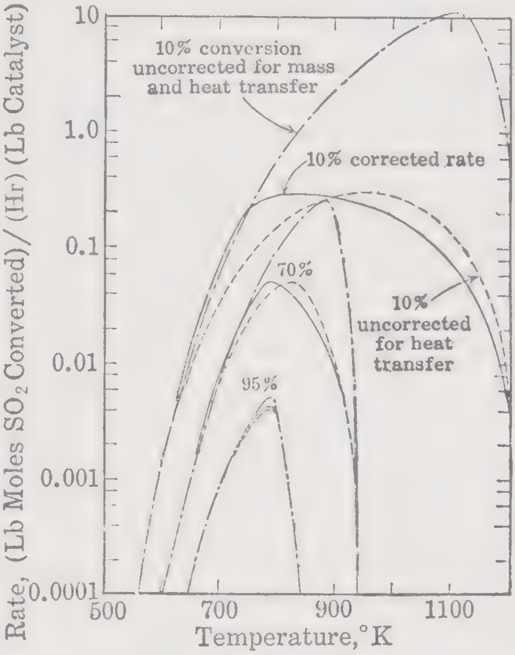


FIG. 199. Effect of Mass and Heat-Transfer Gradients on the Rate of Catalytic Oxidation of Sulfur Dioxide.

Illustration 1 may also be considered as the initial step of a progressive integration for the design of an adiabatic reactor. By similar calculations applied to succeeding increments of reactor volume the variation of composition, pressure, and temperature may be predicted. If change in total pressure is negligible the curve representing the adiabatic operation of a reactor may be plotted on Fig. 198 from the adiabatic heating lines of Fig. 157, page 721. Such a curve is plotted for the reactor of Illustration 1. It may be noted that the rate of reaction rises to a maximum at approximately 30 per cent conversion and falls toward zero at approximately 80 per cent.

It is evident from Fig. 198 that if high conversions are to be reached some means of cooling the reactor must be provided. One scheme is to use two reactors, of which the first is adiabatic and the second is provided with cooling coils so arranged that the temperature may be controlled to follow the curve of maximum rate. For example, the first reactor with the initial conditions of Illustration 1 might be designed to produce a conversion of 52 per cent, where the adiabatic operation curve of Fig. 198 intersects the maximum rate curve. Controlled cooling in the second reactor will permit operation to high conversions along the maximum rate curve. The amount of catalyst required per unit of feed W/F is readily calculated by graphical integration of Equation (XIX-64). Values of $1/r$ read from Fig. 198 are plotted against x to correspond to the selected scheme of temperature control.

An alternate scheme which simplifies the mechanical problems of reactor construction and the replacement of catalyst is the use of a series of adiabatic reactors with controlled intercoolers. For example, as indicated on Fig. 198, the adiabatic operation might be continued to 70 per cent conversion with little loss in rate. An intercooler might then be used to cool to 400°C before entering a second adiabatic reactor which would produce a conversion of 95 per cent operating along the indicated curve. By using more reactors and intercoolers a closer approach to maximum rate operation and higher conversions may be obtained.

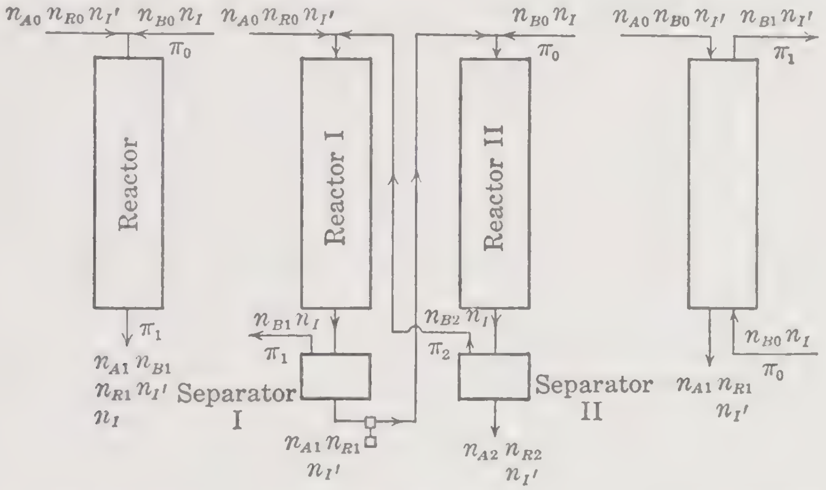
MULTISTAGE OPERATION

There are frequently advantages to be gained in carrying out a reaction in two or more reactors or "stages." In the preceding section the use of multiple reactors simply as a means of temperature control is discussed. In such operations there is no addition or removal of reactants or products between reactors, and the series of reactors may be considered as constituting only a single stage of operation.

True multistage operation may be of either a concurrent or countercurrent type. Concurrent multistage operation is advantageous for polymolecular reactions in which one reactant undergoes undesirable side reactions if it is permitted to exist in high concentrations. For example, in the catalytic alkylation of butane with butenes to produce isomeric octanes the alkylation reaction is accompanied by undesirable polymerization of the olefins. Such side reactions are effectively controlled by successive introductions of the olefin into the isobutane stream so that at no point is there a high concentration of olefins which will produce a high polymerization rate. Multiple-point introduction of a reactant in this manner may be practiced in a series of reactors or by providing multiple-feed points in a single reactor, but in either case it may be considered as a concurrent multistage operation.

Prediction of the operating results of concurrent multistage reactor systems involves no new principles if rate equations are available for all important reactions. Calculations are started from the reactor inlet and carried through the successive stages, each addition of reactants being taken into account.

Where it is desired to produce a high degree of completion of a polymolecular reaction with a minimum of excess reactants it is frequently economical to employ countercurrent multistage operation. For example, in the reaction $A + B \rightleftarrows R$ it may be desired to obtain maximum conversion of the limiting reactant A with minimum excess of reactant B. This would be accomplished in a reactor in which A is continuously contacted with B in counterflow. With this arrangement a maximum concentration of A is present at one end where B is at a minimum, while at the other end B is at a maximum where A is at a minimum. Such a continuous counterflow operation is possible in a single reactor if B is gaseous while A and R are liquid under the conditions of reaction. In the general case where the reactants and products are in a single phase at reaction conditions it is possible to approach continuous counterflow operation by a series of separate reactor stages with separation of the reactants between stages. The practicability of the counterflow operation depends largely upon the difficulty of this separation. Ordinarily it must involve only cooling followed by a simple phase separation of a gas or solid from a liquid or the separation of two immiscible liquids.



Single Stage Two Stage Counter Flow

FIG. 200. Flow Diagrams for Multistage Reactors.

In Fig. 200 are flow diagrams representing single-stage, two-stage counterflow, and continuous counterflow operations for the general reaction $A + B \rightleftarrows R$. A larger number of multiple stages, approaching the effect of continuous counterflow, is obtained by adding intermediate reactors and separators to a two-stage arrangement.

The symbol n on Fig. 200 represents the number of moles of each component, per unit mass of total feed to the system. The diagrams represent operations which are possible if A and R are liquids, associated with a liquid inert component I' and if B is a gas associated with a gaseous inert component I. In such systems the pressure drops in the reactors are determined by the direction of gas flow. Thus, in the two-stage operation $\pi_0 > \pi_2 > \pi_1$, and the indicated pump is necessary to transfer the liquid phase from state I to II. By the addition of suitable heaters and coolers this two-stage operation is feasible with single-phase conditions of the fluid streams in the reactors. An infinite number of such stages would yield the counterflow operation.

If x_A and x'_A represent the conversion of A per mole of total feed to the system in the first and second reactors, respectively, the composition of the system at any point in a reactor is represented by the material-balance equations in Table LXI.

TABLE LXI

MULTISTAGE-REACTOR EQUATIONS

	Single Stage	*Two Stages*		*Counterflow (Infinite Stages)*
		First	*Second*	
n_A	$n_{A0}-x_A$	$n_{A0}-x_A$	$n_{A1}-x'_A$	$n_{A0}-x_A$
n_B	$n_{B0}-x_A$	$n_{B2}-x_A$	$n_{B0}-x'_A$	$n_{B1}+x_A$
n_R	$n_{R0}+x_A$	$n_{R0}+x_A$	$n_{R1}+x'_A$	$n_{R0}+x_A$
n_t	$n_{A0}+n_{B0}+n_{R0}$ $+n_I+n_I'-x_A$	$n_{A0}+n_{B2}+n_{R0}$ $+n_I+n_I'-x_A$	$n_{A1}+n_{B0}+n_{R1}$ $+n_I+n_I'-x'_A$	$n_{A0}+n_{B1}+n_{R0}$ $+n_I+n_I'+x_A$
Overall balances	$n_{B1}=n_{B0}-x_{A1}$	$n_{A1}=n_{A0}-x_{A1}$ $n_{R1}=n_{R0}+x_{A1}$	$n_{B2}=n_{B0}-x'_{A2}$ $n_{A2}=n_{A0}-x_{A1}$ $-x'_{A2}$	$n_{B1}=n_{B0}-x_{A1}$ $n_{A1}=n_{A0}-x_{A1}$

If the pressure drops in the reactors do not significantly affect the reaction rates the amounts of catalyst required in the reactors of a two-stage system are readily calculated by either analytical or graphical integration of Equation (XIX-64) in combination with the reaction rate equations and the material balances of Table LXI. For specified values of x_{A1} and x'_{A2}, the mole fractions of the reactants in each reactor are expressed as functions of the conversions x_A and x'_A. The corresponding activities are then calculated and the integrations completed by the usual methods, thus determining the amount of catalyst required in each reactor. Variations in temperature and pressure in each of the reactors may be taken into account if the inlet conditions are known. If no compressor is used between the stages on the gas stream the pressure at the inlet to the first reactor must be determined by a trial-and-error procedure in which pressure drops are first assumed and then verified by the reactor integration.

This same procedure may be repeated for different values of x_{A1} at a constant over-all conversion $x_{A1} + x'_{A2}$. The results of such a series of calculations may be plotted with weights of catalyst per unit mass of feed W/F as ordinates against x_{A1}, the conversion in the first reactor. A typical set of curves is shown diagrammatically in Fig. 201. It may be noted that the minimum catalyst requirement corresponds to a first-stage reactor approximately 50 per cent larger than the second. However, there are frequently mechanical and operating advantages in building reactors of equal size. In this case the increase in over-all catalyst requirement would be negligible.

The equations corresponding to an infinite number of stages or continuous counterflow are readily integrated if constant temperature and pressure are assumed. The mole fractions throughout the reactor are expressed as functions of x_A by the equations of Table LXI. The size of the reactor is obtained by determining the area under a curve of $1/r_{Am}$ plotted as ordinates against x_A. Where constant pressure and temperature are not assumed the calculations become difficult. In most cases the advantages of more than two counterflow stages are too small to justify the added complexity of the equipment. This conclusion is readily verified by comparing the results of an optimum two-stage system with the hypothetical infinite stage case.

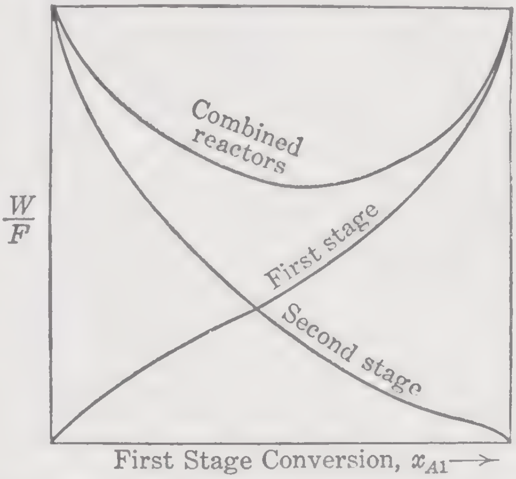


FIG. 201. Catalyst Requirements for a Two-Stage Reactor System.

The economics of multistage operation are reviewed by Kassel[5] who developed design charts for the hydrogenation of butene codimer on the basis of a simplified rate equation which permitted analytical integration.

REACTOR TEMPERATURE CONTROL

In many catalytic operations the most serious design problem is that of providing suitable control of the temperatures in the reactor to approximate optimum conditions. Six fundamentally different methods of temperature control are in more or less common commercial use.

1. The method of dividing the reactor into adiabatic sections with intermediate heat exchangers has already been mentioned. This scheme

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[5] L. S. Kassel, *Ind. Eng. Chem.*, **31**, 275 (1939).

is effective but leads to mechanical complications, particularly in high-temperature reactions.

2. Temperature may be controlled by the addition of an inert *heat carrier* to the reactant stream. Where it can be used steam is a most effective heat carrier because of its high heat capacity and the ease with which it may be separated from gaseous systems by condensation. In some operations the molal ratio of steam to reactants is ten or greater. Under such conditions even a large heat of reaction produces only a small temperature change.

3. Temperature may be controlled by the injection of reactants at various points along the length of the reactor. For example, an exothermic reaction may be controlled by successive additions of a cold reactant.

4. The catalyst may be contained in a heat exchanger so arranged that confining surfaces which are in contact with a heating or cooling medium are in close proximity to all catalyst particles. This method of temperature control depends upon lateral transfer of heat through the catalyst bed at right angles to the direction of flow of the reactants. Because the conditions for heat transfer are relatively poor, it is generally necessary that no catalyst particle be more than 2 in. from a cooling surface if its temperature is to be appreciably affected. The problem of calculating the temperature gradients resulting from such lateral heat transfer is discussed on page 1033.

5. The catalyst bed may be moved in a steady stream through the reactor. Two types of moving-bed reactors are in common use. In the " Thermofor "[6] or TCC catalytic reactor the catalyst is in the form of cylindrical or spherical particles which are permitted to flow slowly downward as a moving solid bed. In the " Fluidized "[7] reactor the catalyst is in the form of a powder which is carried by the reactant stream and forms a relatively dense bed in the reactor in a turbulent fluidized state. In both methods the heat capacity of the catalyst stream is of the same order of magnitude as that of the reactants, and heat may be added to the reactor by preheating the catalyst. Heat may be removed by passing all or part of the catalyst through a cooler and returning it to the reactor or by placing cooling coils in the path of flow in the reactor.

6. What may be termed a regenerative reactor has been developed for use where a carbonaceous catalyst deposit from an endothermic reaction frequently must be removed by oxidation. In this operation the catalyst

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[6] R. H. Newton, G. S. Dunham, T. P. Simpson, *Trans. Am. Inst. Chem. Engrs.*, **41**, 215 (1945).

[7] E. V. Murphree, C. L. Brown, E. J. Gohr, C. E. Jahnig, H. Z. Martin, C. W Tyson, *Trans. Am. Inst. Chem. Engrs.*, **41**, 19 (1945).

bed is used as a heat reservoir to store up heat from the exothermic regeneration period. This heat is then given up to the reactants in the subsequent process period. Good temperature control is possible by this method, but the cycle of operation must be short, and a perfect heat balance must be maintained between the regeneration and process periods.

The design problems in the first three types of systems may be handled by the principles developed in the preceding sections. Where pressure changes are significant the progressive stepwise procedure described on pages 875 to 883 permits simultaneous development of temperature, pressure, and conversion relationships in any adiabatic reactor. If pressure changes are negligible direct graphical integration as indicated in Fig. 197 establishes both conversions and temperatures throughout the reactor. This operation is direct and simple where a chart is available which expresses reaction rate as a function of both temperature and conversion. Integrations for adiabatic reactors are readily carried out from adiabatic operating lines plotted on such a chart.

The problems of lateral heat transfer in the fourth type of reactor are discussed in the following sections. The heat-transfer and temperature-distribution problems of the last two types of reactors involve specialized data or procedures which are not yet generally available.

LATERAL HEAT TRANSFER

For control of the temperature of a catalytic reaction by lateral heat transfer through the bed four different types of reactor arrangement have been used.

1. The catalyst is placed in vertical cylindrical tubes which are surrounded by the heat-exchange medium.
2. The catalytic bed is formed around tubes which carry the heat-exchange medium. Elaborate fins are welded to the tubes to improve heat transfer into the granular bed.
3. The catalyst is placed in flat slabs in the alternate envelopes of a flat-plate heat exchanger of the type commonly used for preheating air for combustion.
4. The catalyst is placed in the annular space between two cylindrical tubes. Heat-exchange medium circulates through the inner and around the outer tube.

Various types of heat-exchange medium may be used with any of these reactor types. Boiling liquids, condensing vapors, circulating liquids, molten salts, and circulating gases have all been used.

For the design of any of these reactors it is necessary to predict the lateral temperature distribution at all cross sections. The magnitude of the lateral temperature differences fixes the diameter or distribution of the tubes, the arrangement of the fins or the thickness of the envelope which is required for specified limits of temperature variation.

The problem of calculating the temperature gradients accompanying lateral heat transfer is made difficult by the complex combinations of mechanisms involved. Some heat is transferred by conduction through the catalyst particles and the intervening fluid, some by the convection and turbulence of the fluid, and some by radiation between the particles. It is evident that what may be termed the *effective thermal conductivity* of the bed is a function of the conductivity of the catalyst particles; their shape, size, and arrangement; the properties of the fluid, its mass velocity, and the temperature; and emissivity of the catalyst. If it is assumed that such an effective conductivity is known in terms of lateral heat-transfer rate per unit area and unit temperature gradients, differential equations may be developed to represent the temperature distributions in catalytic beds of simple geometric shapes. General correlations for predicting effective thermal conductivities must be developed before these relationships become quantitatively useful.

Catalyst in Thin Slabs of Infinite Extent. This case is approximated in the flat-plate type of reactor previously described. It is assumed that the temperatures of the confining surfaces on each side of the bed are equal and known at each lateral cross section. The conditions in any lateral section at a distance Z from the inlet are shown diagrammatically in Fig. 202 for a reactor in which the flow of the fluid is downward, parallel to the confining walls. An elementary section dZ in height and dX in thickness is located at a distance X from the center line of the bed. For a bed section of unit width the volume of this element is $dX\,dZ$. If the longitudinal transfer of heat by any means other than the heat capacity of the flowing fluid is neglected, the rates of heat transfer to and from the element are represented by the following equations corresponding to the symbols on Fig. 202.

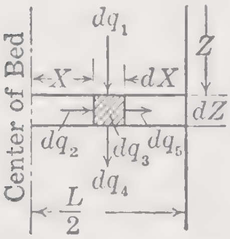

FIG. 202. Lateral Heat Transfer in Thin Slabs.

$$dq_1 = GC_p t\,dX \tag{27}$$

$$dq_4 = GC_p\left(t + \frac{\partial t}{\partial Z}\,dZ\right)dX \tag{28}$$

$$dq_2 = -k\,dZ\,\frac{\partial t}{\partial X} \tag{29}$$

$$dq_5 = -k\,dZ\,\frac{\partial\left(t + \frac{\partial t}{\partial X}\,dX\right)}{\partial X}$$

$$= -k\,dZ\left(\frac{\partial t}{\partial X} + \frac{\partial^2 t}{\partial X^2}\,dX\right) \tag{30}$$

$$dq_3 = -\,r_A\rho_B\Delta H_A\,dX\,dZ \tag{31}$$

where

G = mass velocity
C_p = mean heat capacity per unit mass of fluid
k = effective lateral thermal conductivity of the catalyst-bed fluid system
r_A = rate of reaction, moles of A per unit mass of catalyst
ΔH_A = heat of reaction per mole of A
ρ_B = bulk density of catalyst bed

The energy balance is expressed by

$$dq_1 + dq_2 + dq_3 = dq_4 + dq_5 \tag{32}$$

Substituting Equations (27–31) in (32) gives

$$\left.\begin{aligned} &\left(\frac{\partial t}{\partial Z}\right)_X = A\left(\frac{\partial^2 t}{\partial X^2}\right) + B \\ &\text{where} \\ &A = k/GC_p \\ &B = -\,\frac{r_A\rho_B\Delta H_A}{GC_p} \end{aligned}\right\} \tag{33}$$

Direct integration of Equation (33) is made difficult by the complex variation of B with temperature and conversion x_A which in turn vary with both Z and X.

Catalyst in Cylindrical Tubes. The conditions in a catalyst bed inside a cylindrical tube are shown diagrammatically in Fig. 203. This case differs from that of the flat slab in that the heat flow is radial, through a cross section of varying area. The following equations similar to (26–33) represent the rates of heat transfer into and out of an elementary ring of height dZ, radial thickness dX, and radius X.

$$dq_1 = GC_pt\,2\pi X\,dX \tag{34}$$

$$dq_4 = GC_p\left(t + \frac{\partial t}{\partial Z}\,dZ\right)2\pi X\,dX \tag{35}$$

$$dq_2 = -k\left(\frac{\partial t}{\partial X}\right)2\pi X\,dZ \tag{36}$$

$$dq_5 = -k\,\frac{\partial\left(t + \dfrac{\partial t}{\partial X}\,dX\right)}{\partial X}\,2\pi(X + dX)\,dZ \tag{37}$$

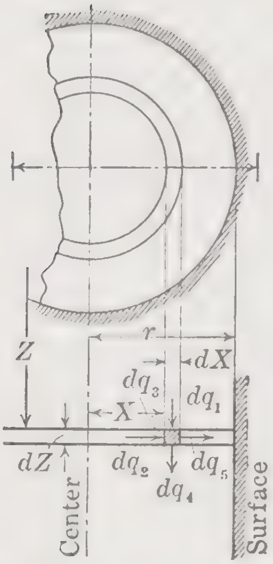

FIG. 203. Lateral Heat Transfer in a Cylindrical Reactor.

$$dq_3 = -\,r_A\rho_B\Delta H_A 2\pi X\,dX\,dZ \tag{38}$$

$$dq_1 + dq_2 + dq_3 = dq_4 + dq_5 \tag{39}$$

Combining and simplifying yields

$$\left(\frac{\partial t}{\partial Z}\right)_X = A\left[\frac{\partial^2 t}{\partial X^2} + \frac{1}{X}\,\frac{\partial t}{\partial X}\right] + B \tag{40}$$

where A and B are the same as in Equation (33).

Equations similar to (27–40) can also be developed for mass transfer. Thus, for a cylindrical reactor,

$$\left(\frac{\partial p_A}{\partial Z}\right)_X = \left(\frac{D'_{Am}p}{p - p_A}\right)\left(\frac{M_m p}{RT}\right)\left[\frac{\partial^2 p_A}{\partial X^2} + \frac{1}{X}\left(\frac{\partial p_A}{\partial X}\right)\right]_Z - \frac{r_A\rho_B M_m p}{G} \tag{41}$$

Use of Equation (41) is made difficult by uncertainty as to the proper effective diffusivity D'_{Am} to be used for a fluid moving through the voids of a catalyst bed.

Double Stepwise Integration. Grossman[8] has presented a double stepwise method of integrating Equations (33) and (40) which is based upon the use of small but finite increments. The equations are written in incremental notation as follows:

For thin slabs:

$$\Delta_z t = \frac{A\,\Delta Z}{(\Delta X)^2}\,(\Delta_x^2 t) + B\,\Delta Z \tag{42}$$

For cylindrical reactors:

$$\Delta_z t = \frac{A\,\Delta Z}{(\Delta X)^2}\left(\Delta_x^2 t + \frac{\Delta X}{X}\,\Delta_x t\right) + B\,\Delta Z \tag{43}$$

where $\Delta_z t$ denotes the change of temperature in the longitudinal incremental distance ΔZ and $\Delta_x t$ denotes the change of temperature in the lateral or radial distance ΔX.

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[8] L. A. Grossman, *Trans. Am. Inst. Chem. Engrs.*, **42**, 535 (1946).

The term B of Equations (33–43) involves the reaction rate r_A which is determined by the temperature and activities at the interface of the catalyst particle. Where diffusional and temperature differences between the fluid and the catalyst are negligible a general relationship between B and the average temperature and conversion in the fluid stream is readily derived from the rate equation. Where these gradients cannot be neglected it is necessary to develop a chart similar to Fig. 198 which expresses reaction rate as a function of the average properties of the fluid stream but is restricted to a single mass velocity. It is thus possible to present graphically both A and B as functions of the average temperature and conversion x_A in the fluid stream at any point, even though the relationships may be very complex. Such charts are shown in Figs. 205–207 for the system of Illustration 2. The values of B and A in Equations (42) and (43) are properly based on the mean temperature and conversion existing over the increment ΔZ at the position under consideration.

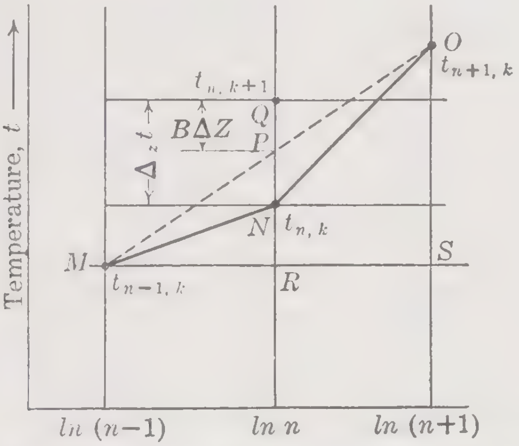

FIG 204. Graphical Calculation of Temperature in a Cylindrical Reactor.

The conversion $\Delta_z x_A$ produced in any increment of length Z is expressed by

$$\Delta_z x_A = \frac{r_A \rho_B \Delta Z S}{F} \tag{44}$$

where S = total cross-sectional area of reactor
F = reactor feed rate
r_A = rate of reaction at the average temperature and conversion of the increment ΔZ, moles/(mass of catalyst) (time)

The stepwise solution of Equations (42) and (43) is facilitated by maintaining the following definite relationship between the lateral and longitudinal dimensions of each incremental volume considered:

$$\Delta Z = \frac{(\Delta X)^2}{2.1} \tag{45}$$

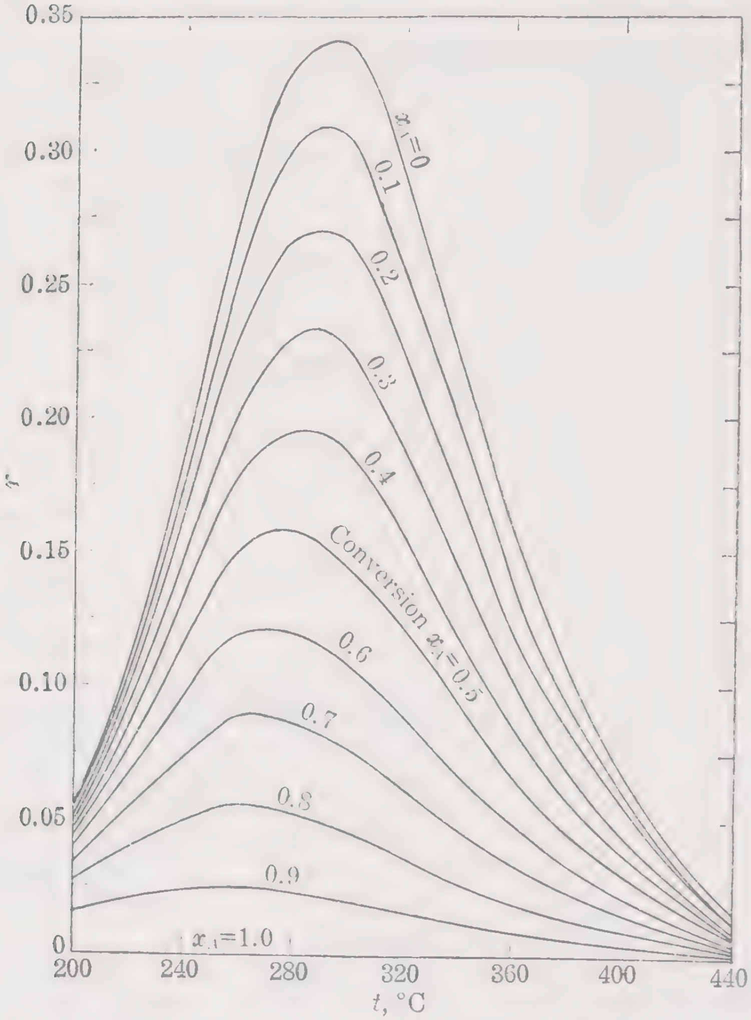

FIG. 205. Effect of Temperature and Conversion on a Specific Catalytic Reaction Rate.

With this restriction Equations (42) and (43) become

$$\text{(Slabs)}\ \Delta_z t = \frac{1}{2}\,(\Delta_x^2 t) + B\,\Delta Z \tag{46}$$

$$\text{(Cylinders)}\ \Delta_z t = \frac{1}{2}\left(\Delta_x^2 t + \frac{\Delta X}{X}\,\Delta_x t\right) + B\,\Delta Z \tag{47}$$

In applying Equations (46) and (47) the lateral or radial dimension of the reactor is divided into n small but finite equal increments ΔX. Then,

$$X = n\,\Delta X \tag{48}$$

The longitudinal dimension of the reactor is divided into k small increments ΔZ whose lengths are not necessarily equal but are related to the corresponding values of ΔX through Equation (45). Then, if the lateral gradients about any point Z, X corresponding to increment k, n, are considered:

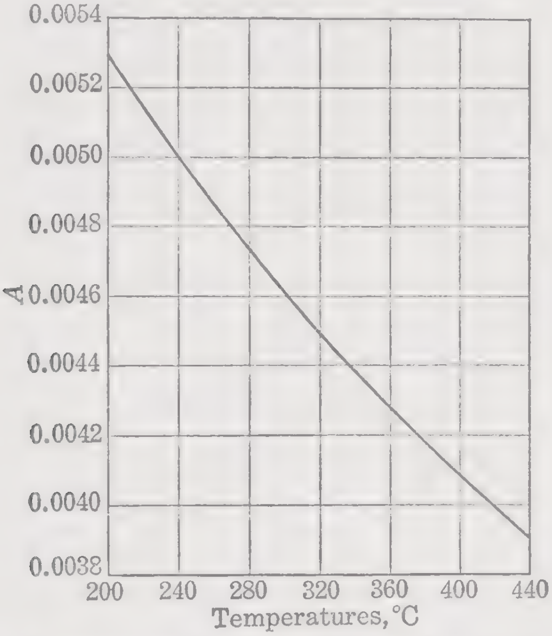

FIG. 206. Effect of Temperature on Factor A in a Specific Catalytic Reaction.

$$\Delta_z t = t_{n,\,k+1} - t_{n,\,k} \tag{49}$$

$$\Delta_x t = \tfrac{1}{2}(t_{n+1,\,k} - t_{n-1,\,k}) \tag{50}$$

$$\Delta_x^2 t = (t_{n+1,\,k} - t_{n,\,k}) - (t_{n,\,k} - t_{n-1,\,k}) \tag{51}$$

where $t_{n,\,k+1}$ indicates the temperature at a point $(Z + \Delta Z)$, X and $t_{n+1,\,k}$ indicates the temperature at a point Z, $(X + \Delta X)$. Combining Equations (48–51) with (46–47) gives:

For slabs:

$$\Delta_z t = \tfrac{1}{2}(t_{n+1,\,k} + t_{n-1,\,k} - 2t_{n,\,k}) + B\,\Delta Z \tag{52}$$

For cylinders:

$$\Delta_z t = \tfrac{1}{2}\left[t_{n+1,\,k} + t_{n-1,\,k} - 2t_{n,\,k} + \frac{1}{2n}(t_{n+1,\,k} - t_{n-1,\,k})\right] + B\,\Delta Z \tag{53}$$

If the lateral temperature distribution is known at some starting point such as the reaction inlet Equations (52) and (53) permit direct calculation of the successive increments in longitudinal temperature corresponding to the lateral position X of each of the selected increments ΔX. However, the longitudinal temperature increments so calculated do not correspond to uniform increments in ΔZ, and Equation (45) must be successively used to establish the value of Z corresponding to each temperature.

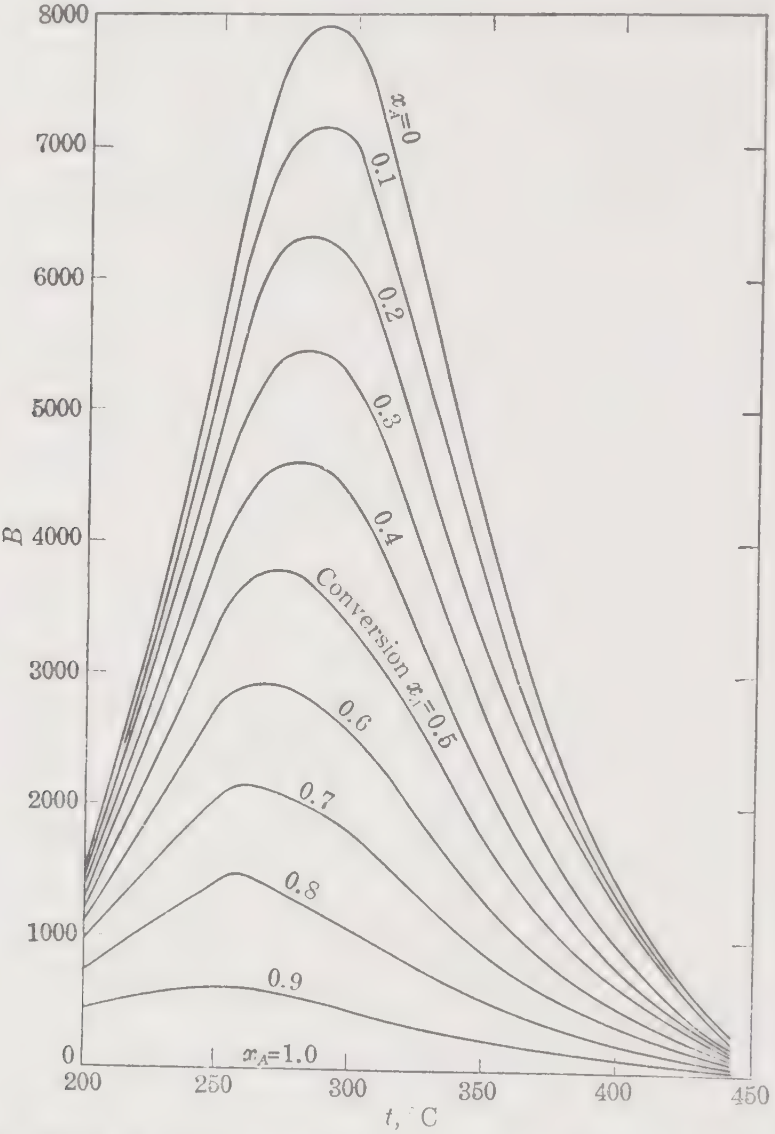

Fig. 207. Effect of Temperature and Conversion on Factor B in a Specific Catalytic Reaction.

Grossman developed the successive solution of Equations (52) and (53) for both slabs and cylinders by a graphical procedure similar to the general method of Schmidt[9,10] for heat-transfer calculations in the unsteady state in slabs. This procedure is demonstrated in Fig. 204 for the case of a cylindrical reactor involving Equation (53). The radius of the reactor is divided into equal increments ΔX and on the abscissa scale of Fig. 204 are plotted values of ln n where n is the number of the increment, starting with zero at the center. Thus, the center of the reactor corresponds to negative infinity on this scale while the zero point represents the first increment at a distance ΔX from the center. Figure 204 illustrates the gradients about a typical increment number n for an endothermic reaction under conditions such that the temperature of the fluid stream is being increased by heat transfer from the walls of the reactor.

It may be shown from the geometry of Fig. 204 that the distance PN is equal to one half of the terms inside the brackets of Equation (53) and that QP is therefore equal to $B\,\Delta Z$. Thus,

$$\frac{RP}{SO} = \frac{MR}{MS} = \frac{\ln(n) - \ln(n-1)}{\ln(n+1) - \ln(n-1)} = \frac{\ln\dfrac{n}{n-1}}{\ln\dfrac{n+1}{n-1}} \approx \frac{1}{2} + \frac{1}{4n} \tag{54}$$

Then,

$$PN = RP - RN = SO\left(\frac{1}{2} + \frac{1}{4n}\right) - RN \tag{55}$$

or

$$\begin{aligned} PN &= (t_{n+1,\,k} - t_{n-1,\,k})\left(\frac{1}{2} + \frac{1}{4n}\right) - (t_{n,\,k} - t_{n-1,\,k}) \\ &= \frac{1}{2}\left[t_{n+1,\,k} + t_{n-1,\,k} - 2t_{n,\,k} + \frac{1}{2n}(t_{n+1,\,k} - t_{n-1,\,k})\right] \end{aligned} \tag{56}$$

Comparison of Equations (56) and (54) shows that point Q on Fig. 204 may be established by graphically locating point P and adding the temperature increment $B\,\Delta Z = PQ$. Since the value of B should be based on the average temperature and conversion over the increment ΔZ it may be necessary to evaluate it by successive trials, if the changes per increment are large. The change in conversion is expressed by a combination of Equations (44) and (45).

$$\Delta_z x_A = \frac{r_A \rho_B (\Delta X)^2 S}{2AF} \tag{57}$$

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[9] E. Schmidt, *Beitr. Tech. Mechanik und Tech. Physik*, pp. 179–89 (1924).

[10] E. Schmidt, *Forsch. Gebiete Ingenieurw.*, 13, 177–84 (1942).

This procedure is repeated for each increment across the reactor, thus establishing a temperature-distribution curve corresponding to the longitudinal increment $k + 1$. The corresponding ΔZ values are calculated from Equation (45) to permit a plot of Z against temperature and conversion for each radial position.

It is readily demonstrated that Equation (52) may be solved by a graphical procedure similar to that of Fig. 204, except that the abscissas are increment numbers n plotted on a uniform scale instead of $\ln(n)$.

At the center of either a slab or a cylindrical reactor where $n = 0$ the temperature $t_{(k+1)(n=0)}$ at a value of Z corresponding to increment $(k + 1)$ is approximated by adding the proper mean value of $B\,\Delta Z$ to the temperature $t_{k(n=1)}$. For obtaining the value of $t_{(k+1)(n=1)}$ in a cylindrical reactor the appropriate value of $B\,\Delta Z$ is added to the value of $t_{k(n=2)}$. This is equivalent to making line OPM of Fig. 204 horizontal from $\ln(2)$ to negative infinity in order to locate point P where $n = 1$.

This method of calculation neglects lateral mixing of the fluid flowing through the bed as well as all diffusion or mixing in a longitudinal direction. It is also assumed that the mass velocity is uniform across the entire cross section of the reactor. Although these assumptions are not rigorous it is probable that the error they contribute is small in comparison to the uncertainty of the effective thermal conductivity k.

Illustration 2. In a hydrogenation operation an olefinic vapor is charged to a catalytic reactor with 1.2 moles of hydrogen per mole of olefin. The mixture enters the reactor at 200°C and 5 atm at such a mass velocity that partial pressure and temperature differences between the fluid stream and the catalyst are negligible. The effective thermal conductivity k of the gas–solid system is estimated to be 0.5 Btu/(hr)(ft)(°F). The catalyst is contained in cylindrical tubes having an internal diameter of 1.25 in. The walls of the tube are surrounded by boiling water at a temperature of 200°C. It is desired to calculate the temperature and conversion gradients throughout a representative tube.

From the catalytic rate equation the rates of reaction in pound-moles of olefin reacted per hour per pound of catalyst were calculated at various temperatures and conversions and plotted in Fig. 205. It may be noted that this reaction rate passes through a maximum as temperature is increased. This retardation of the reaction rate occurs at temperatures far below that at which the reverse reaction becomes appreciable.

Based on the rate relationships of Fig. 205, the thermochemistry of the reaction, and the physical properties of the system, the values of A and B in Equations (33) and (40) were calculated at various temperatures and conversions and plotted in Figs. 206 and 207, respectively. The effect of conversion on A is negligible. The feed rate and catalyst-bed density are such that Equation (57) becomes

$$\Delta_z x_A = \frac{31.8(\Delta X)^2 r_A}{A} \tag{a}$$

The method of graphical calculation based on Equation (53) and Fig. 204 is demonstrated in Fig. 208 for the increments $k = 1$, 2, and 7, corresponding to five equally spaced radial positions extending from the center of the tube where $n = 0$ to the wall where $n = 5$. The lines used in the calculations for the longitudinal increments $k = 3$, 4, 5, and 6 are omitted from Fig. 208 for simplification, although it is evident that they must be carried out in order to establish the gradient at $k = 6$.

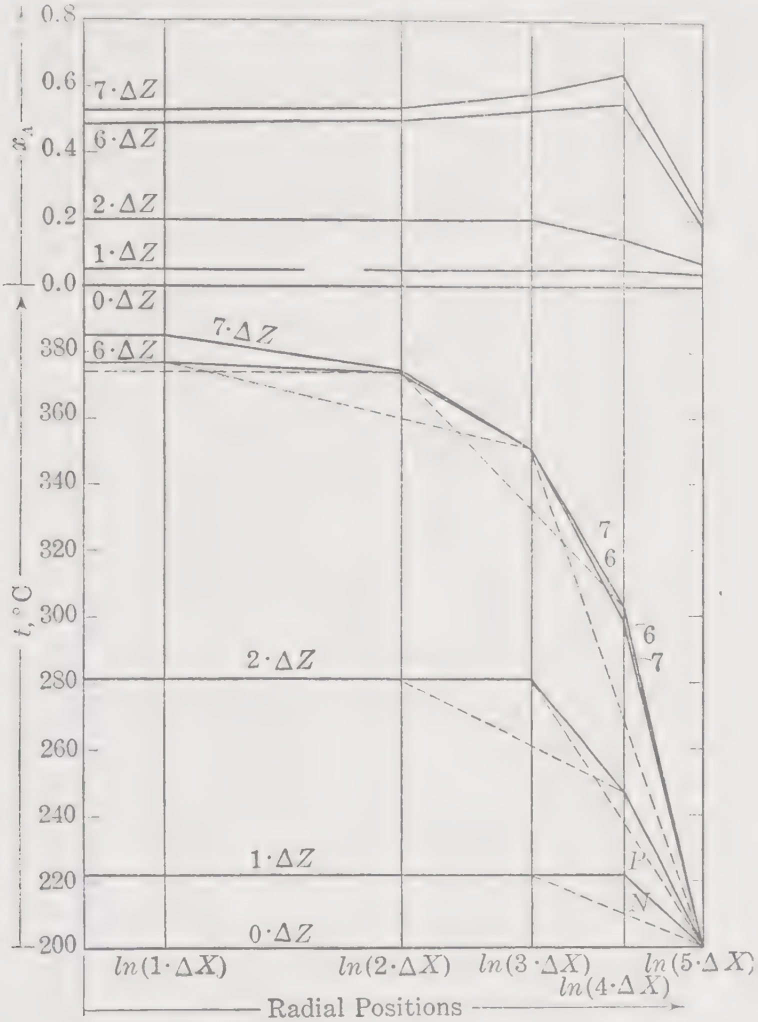

FIG. 208. Graphical Method of Calculating Temperature and Conversion Gradients in a Cylindrical Reactor.

Since $\Delta X = (1.25)/(12)(5)(2) = 0.0104$ ft, Equation (45) becomes,

$$\Delta Z = \frac{(0.0104)^2}{2A} = \frac{54.1\ (10^{-6})}{A} \tag{b}$$

and Equation (a) becomes

$$\Delta_z x_A = \frac{0.00344\ r_A}{A} \tag{c}$$

At the reactor inlet $Z = 0$, $k = 0$, $t = 200$, and $x_A = 0$ for all radial positions. Over the interval from $k = 0$ to $k = 1$ a mean temperature of 211°C and a mean conversion of 0.026 are assumed for a first trial calculation at all radial positions except at the wall ($n = 5$) where t is kept constant at 200°C and a mean conversion of 0.019 is assumed. Values of r_A, A, and B are read from Figs. 205–207 for these conditions.

	$n = 0, 1, 2, 3, 4$	$n = 5$
r_A	0.078	0.055
A	0.00522	0.00528
B	2140	1500
$\Delta_z x_A$, Equation (a)	0.0514	0.0358
ΔZ, Equation (b)	0.0103	0.0103
$B\ \Delta Z$	22.3	....

The temperatures at $k = 1$ are hence $200 + 22.3 = 222.3$°C for all radial positions except at the surface which is at 200°C, and conversions are 0.051 for all radial positions except at the surface which is 0.036. The mean temperatures for all positions except the surface are 211 in agreement with the assumed value, and the mean conversion is 0.025 at all positions except at the surface which is 0.019, both in agreement with the assumed values; the calculated values are hence correct. These calculations are summarized in Table A.

Similar calculations are repeated for the second increment of ΔZ from $k = 1$ to $k = 2$. Since values of temperature at $k = 1$ and radial positions $n = 1$, 2, 3, and 4 are the same $\Delta_z t = B\ \Delta Z$ in the first three radial positions. At the radial positions 4 and 5 the temperatures are determined by adding values of $B\ \Delta Z$ from Table A to the points determined by the intersections of the lines on Fig. 208. These calculations are repeated for succeeding increments as indicated in Table A and Fig. 208.

Values of temperature and conversion for given radial positions in Table A are plotted against longitudinal distance Z in Fig. 209. In this figure the mean and adiabatic lines as well as all radial lines are shown for both temperature and conversion. The mean values of t and x_A were obtained by graphical integration from 0 to X^2 from a cross-plot of the six radial positions against X^2.

The foregoing procedure may seem extremely laborious, especially in securing agreement between assumed and calculated mean values of temperature and conversion; however, the first trial values can be made satisfactory after the first few increments of ΔZ have been passed by plotting t and x_A against k and extrapolating to the next half interval of ΔZ. The greatest difficulty occurs where the temperature gradients begin to reverse in direction as shown in the range of $k = 6$.

Unexpectedly high radial temperature gradients are shown in Fig. 209. The mean temperature line occurs at a radial position of about 0.7 of the radius and a mean conversion at a radial position of about 0.5. It is particularly interesting to note that the maximum conversion occurs at a radial position of 0.8 rather than at the center of the tube.

In this analysis no allowance was made for radial diffusion of gases, and the value of thermal conductivity is uncertain. The method can be extended to include diffusion effects. At present there are no published data on either thermal conductivity or diffusion of fluid streams flowing through granular solids. Much experimental work is needed in this field.

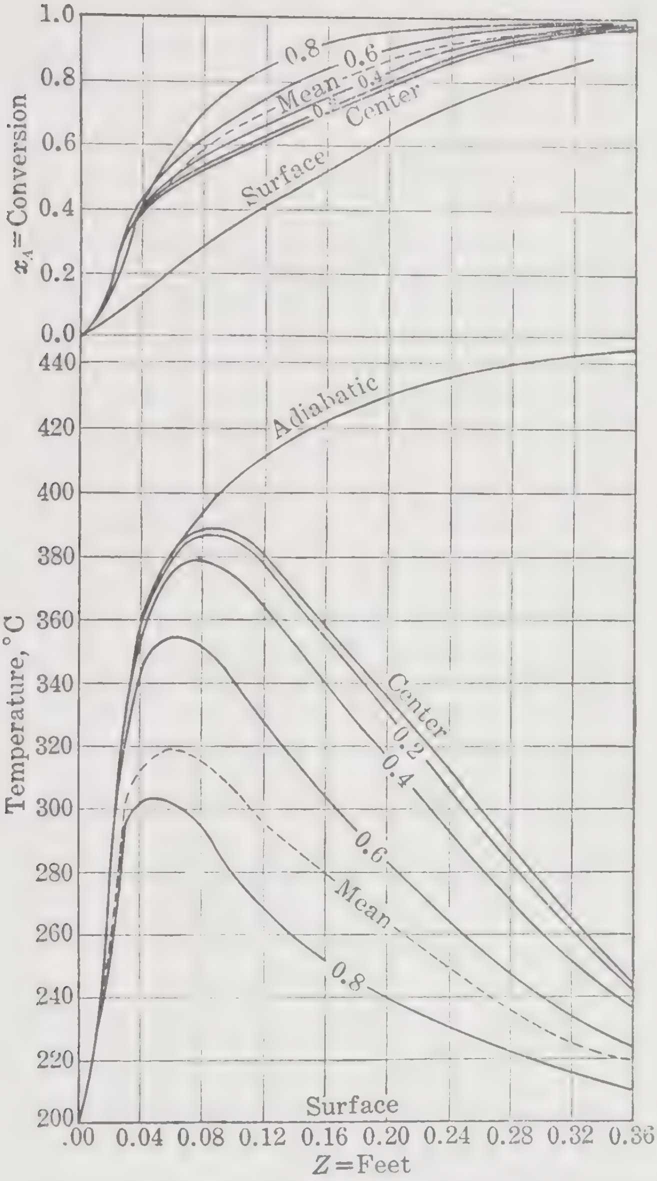

FIG. 209. Conversion and Temperature Gradients in a Cylindrical Reactor.

TABLE A

Calculation of Temperature and Conversion Gradients in a Cylindrical Reactor

Radial Positions n	t_{in}	t_m *(trial)*	x_A in	x_m *(trial)*	A	ΔZ	B	r_A	$B\,\Delta Z$ *(trial)*	Δx_A	Z	t_m *(calc.)*	x_m *(calc.)*
$k = 0$ to 1													
Center 0	200°	....	0	.....	.....	.....	....	.....	....	....	0	....	....
	....	211°	.....	0.025	0.00522	0.0103	2140	0.078	22.3°	0.0514	....	211°	0.026
1	200°	....	0	.....	.....	.....	....	.....	....	....	0	....	....
	....	211°	.....	0.025	0.00522	0.0103	2140	0.078	22.3°	0.0514	....	211°	0.026
2	200°	....	0	.....	.....	.....	....	.....	....	....	0	....	....
	....	211°	.....	0.025	0.00522	0.0103	2140	0.078	22.3°	0.0514	....	211°	0.026
3	200°	....	0	.....	.....	.....	....	.....	....	....	0	....	....
	....	211°	.....	0.025	0.00522	0.0103	2140	0.078	22.3°	0.0514	....	211°	0.026
4	200°	....	0	.....	.....	.....	....	.....	....	....	0	....	....
	....	211°	.....	0.025	0.00522	0.0103	2140	0.078	22.3°	0.0514	....	211°	0.026
Surface 5	200°	.....	0	0.019	0.00528	0.0103	1500	0.055	....	0.0358	0	200°	0.019
$k = 1$ to 2													
Center 0	222°	....	0.051	.....	.....	.....	....	.....	....	....	0.0103	....	....
	.. .	251°	.....	0.125	0.00493	0.0110	5350	0.210	59.0°	0.146	....	251°	0.125
1	222°	....	0.051	.....	.....	.....	....	.....	....	....	0.0103	....	....
	....	251°	.....	0.125	0.00493	0.0110	5350	0.210	59.0°	0.146	....	251°	0.125
2	222°	....	0.051	.....	.....	.....	....	.....	....	....	0.0103	....	....
	....	251°	.....	0.125	0.00493	0.0110	5350	0.210	59.0°	0.146	....	251°	0.125
3	222°	....	0.051	.....	.....	.....	....	.....	....	....	0.0103	....	....
	....	251°	.....	0.125	0.00493	0.0110	5350	0.210	59.0°	0.146	....	251°	0.125
4	222°	....	0.051	.....	.....	.....	....	.....	....	....	0.0103	....	....
	....	235°	.....	0.097	0.00506	0.0107	3490	0.135	37.2°	0.092	....	235°	0.097
Surface 5	200°	....	0.036	0.054	0.00528	0.0103	1500	0.057	....	0.037	0.0103	200°	0.054
$k = 2$ to 3													
Center 0	281°		0.197								0.0213		
1	281°		0.197								0.0213		
2	281°		0.197								0.0213		
3	281°		0.197								0.0213		
4	247°		0.143								0.0210		
Surface 5	200°		0.073								0.0206		
$k = 6$ to 7													
Center 0	380°	....	0.480	.....	.....	.....	....	.....	....	....	0.0590	....	....
	....	384°	.....	0.503	0.00417	0.0130	950	0.058	12.4°	0.0479	....	382°	0.504
1	377°	....	0.491	.....	.....	.....	....	.....	....	....	0.0584	....	....
	....	382°	.....	0.515	0.00417	0.0130	1000	0.058	13.0°	0.0429	....	382°	0.515
2	374°	....	0.499	.....	.....	.....	....	.....	....	....	0.0583	....	....
	....	375°	.....	0.52	0.00420	0.0129	1050	0.049	13.5°	0.040	....	375°	0.519
3	352°	....	0.533	.....	.....	.....	....	.....	....	....	0.0567	....	....
	....	351°	.....	0.56	0.00433	0.0125	1450	0.068	18.2°	0.054	....	351°	0.560
4	303°	....	0.555	.....	.....	.....	....	.....	....	....	0.0547	....	....
	....	301°	.....	0.595	0.00458	0.0118	2550	0.106	29.7°	0.0792	....	301°	0.595
Surface 5	200°	....	0.182	0.198	0.00528	0.0103	1450	0.050	.....	0.0325	0.0515	200°	0.198

$k = 7$ to 8

Center 0	389°		0.528								0.0720		
1	387°		0.525								0.0714		
2	375°		0.539								0.0712		
3	351°		0.587								0.0692		
4	299°		0.644								0.0665		
Surface 5	200°		0.214								0.0618		

PROBLEMS

1. The nickel catalyst of Illustration 2, Chapter XIX, is to be used for the hydrogenation of butene codimer in a single-stage isothermal reactor operating at a gauge pressure of 150 lb per sq in. Pure hydrogen is fed in 40 per cent excess of that required for complete reaction, the remainder being recycled. Neglecting mass and heat-transfer effects and pressure drop, calculate by graphical integration the weight of catalyst which must be supplied per pound-mole of codimer fed per hour in order to produce 99.8 per cent hydrogenation at an inlet temperature of:

(*a*) 250°F.
(*b*) 350°F.

The reverse reaction may be neglected.

2. Repeat problem 1 for an adiabatic reactor in which hydrogenated product is recycled for temperature control in the ratio of two moles of hydrogenated product per mole of codimer feed. Hydrogen is supplied in 40 per cent excess of that required to hydrogenate the olefins in the feed. It is desired that the total product shall be 99.8 per cent hydrogenated codimer. Determine the catalyst–feed ratio for the following inlet temperatures:

(*a*) 275°F
(*b*) 300°F

3. Hurt[1] found that the oxidation of a gas containing 7.8 per cent SO_2, 10.8 per cent O_2 and 81.4 per cent N_2 over a catalyst in the form of $\frac{3}{8}'' \times \frac{3}{8}''$ pellets is represented by the following equation for the height of a reactor unit H_R in inches,

$$H_R = [1 + k_1(p_{SO_3})](H_d + H_c)$$

where H_d = height of a transfer unit at average conditions, inches
p_{SO_3} = average partial pressure of SO_3, atm
$H_c = e^{\frac{13,000}{T} - 16.89}$ (in.) = height of a catalytic unit at a mass velocity of 600 lb/(sq ft)(hr) and a pressure of 1.0 atm
$k_1 = e^{\frac{6100}{T} - 5.84}$ (1/atm)

Calculate the depth of the catalyst bed required to produce 95 per cent oxidation of the SO_2 in an isothermal reactor operating at a temperature of 450°C and 1.8 atm with a mass velocity of 500 lb/(hr)(sq ft). The pressure drop in the bed may be neglected, and the average height of a transfer unit may be calculated by consideration of the diffusion of only SO_2, if zero concentration is assumed at the interface.

4. A catalyst in the form of $\frac{3}{16}'' \times \frac{3}{16}''$ cylinders is found to pack with a void fraction of 0.345 in random dense arrangement. A mixture of 10 mole per cent butene−2 with 90 per cent steam is passed at a mass velocity of 620 lb/(sq ft)(hr) through the bed at an inlet temperature of 1200°F and an absolute pressure of 24 lb per sq in.

(*a*) Calculate the pressure drop in pounds per square inch per foot of bed depth at the inlet conditions if the bed is packed in a dense arrangement.

(*b*) Repeat the calculation of part (*a*) for a bed in a loose arrangement having void fraction of 0.42.

5. Calculate the pressure drop in pounds per square inch per foot of bed depth at the inlet conditions of the reactor of problem 5 of Chapter XX if the bed is in random dense arrangement with a 36 per cent void volume.

6. Calculate the pressure drop in pounds per square inch per foot of bed depth in the reactor of problem 6 of Chapter XX if the catalyst when in dense arrangement has 36 per cent void volume.

7. It is proposed to dehydrogenate *n*-butane to produce 35 per cent conversion in a catalytic reactor operating at a temperature of 1050°F with an absolute pressure of 200 mm of Hg at the outlet and an inlet pressure of 375–425 mm of Hg. It is known that under these conditions considerable yields of butadiene are obtained, but this secondary reaction and the accompanying pyrolysis may be neglected and the reaction assumed to follow Equations (XIX-94–98). The catalyst bed has the same density and void volume as that of problem 6, Chapter XX.

(*a*) Assuming isothermal operation and neglecting mass-transfer effects, determine the space velocity required by a graphical integration of the type of Fig. 197, based on an assumed pressure distribution.

(*b*) Calculate the depth of bed corresponding to the specified pressures and the space velocity of part (*a*).

(*c*) Based on the bed depth and mass velocity of parts (*a*) and (*b*), calculate the pressure distribution in the reactor.

(*d*) Correct the space velocity calculated in part (*a*) by a second integration based on the corrected pressure distribution of part (*c*). If a large correction is involved, parts (*b*) and (*c*) should be repeated.

8. Consider the reactor of problem 2 which corresponds to an inlet temperature of 275°F as built in the form of a vertical cylindrical bed 10 ft in depth. The pellet density of the catalyst is 3.5 g per cc, and it is placed in the bed in a random dense arrangement with 36.5 per cent void volume. Retaining this bed depth and with the mass velocity fixed by these conditions, develop a corrected determination of catalyst–feed ratio which takes into account the effects of heat and mass transfer, and pressure drop.

The pressure drop per foot of bed depth may be calculated for both the inlet and outlet conditions of composition and temperature, if a mean gauge pressure of 150 lb per sq in. is assumed. The total pressure drop may then be based on an average of these two values. From the inlet and outlet pressures calculated on this basis construct an approximate curve which relates pressure to bed depth and conversion and conforms to the calculated pressure drop per unit length at the inlet and outlet.

The rate of reaction based on correct interfacial partial pressures and temperatures should be calculated at the inlet conditions and at the conditions corresponding to approximately the maximum rate encountered in the reactor. From these points a complete corrected rate curve is estimated by the principle of Equation (5).

9. Calculate the rate of reaction for the system of Illustration 1 and Fig. 198 at a temperature of 825°K and a conversion of 70 per cent.

10. From the data of Fig. 198 plot curves relating conversion to the catalyst-feed ratio W/F in lb/(lb-mole)(hr) for reactors operating under the following conditions:

(*a*) Temperature control to produce maximum rate at all conversions.

(*b*) Adiabatic operation from 0 to 52 per cent conversion with an inlet temperature of 673°K followed by temperature control to maintain maximum rate at higher conversions.

(*c*) Isothermal operation at 750°K.

(*d*) Single-stage adiabatic operation with an inlet temperature of 673°K.

(*e*) Two-stage adiabatic operation with an intercooler. The inlet temperature for the first stage is 673°K, whereas that for the second stage is 700°K with a conversion of 70 per cent.

11. If the catalyst of problem 10 has a bulk density of 52 lb per cu ft and is arranged in a bed having a random dense arrangement with 36 per cent void volume, calculate the dimensions of the vertical cylindrical beds required for the two-stage operation of part (*e*) with an ultimate conversion of 95 per cent. Calculate the pressure drop through each bed.

12. It is desired to hydrogenate butene codimer over the nickel catalyst of Illustration 2 of Chapter XIX at a gauge pressure of 100 per sq in. and a temperature of 350°F. The catalyst is placed in small-diameter tubes which are surrounded by boiling water held under a suitable pressure for temperature control. The operation may be treated as isothermal, and pressure drops, diffusional gradients, and temperature differences between the catalyst and vapors may be neglected.

The liquid charge is 100 per cent butene codimer while the source of hydrogen is a methane–hydrogen mixture containing 80 mole per cent H_2. It is desired to produce 99.8 per cent saturation of the codimer with an excess of hydrogen of 5 per cent above that required for complete saturation.

Calculate the weight of catalyst for a codimer feed rate of 1 bbl (42 gal) per hr in each of the following systems:

(*a*) A single-stage reactor.

(*b*) A hypothetical counterflow or infinite-stage operation.

(*c*) A two-stage counterflow operation, if complete separation of the hydrogen and methane from the liquid in the separators is assumed. Calculate the weights of catalyst in each stage and the combined weight with conversions of 20, 40, 60, and 80 per cent in the first stage. Graphically estimate the optimum first-stage conversion, and compare the corresponding minimum quantity of catalyst with the results of parts (*a*) and (*b*).

13. Normal butane is to be dehydrogenated in the reactor described in problem 6 of Chapter XX. Assuming that the catalyst bed is at a uniform temperature of 1075°F throughout, calculate by a stepwise integration from Equations (XIX-94–100) the conversion and selectivity resulting from the operation with an inlet temperature of 1075°F and an inlet gauge pressure of 20 lb per sq in. The effects of mass and heat transfer between the fluid and the catalyst particles may be neglected.

14. It is desired to investigate the possibility of dehydrogenating butane in a three-stage adiabatic reactor with interheaters between the stages. Each stage is to produce 10 per cent conversion of the butane in the original feed. The temperature at the inlet to each stage is to be maintained at 1125°F. The gauge pressures at the inlets to the reactors are, respectively, 23, 13, and 3 lb per sq in. Neglecting the effects of mass and heat transfer and assuming applicability of Equations (XIX-94–100), calculate the catalyst–feed ratio, W/F, for each stage and the conversion selectivity relationships throughout. The density and void volume of the catalyst bed are the same as those specified in problem 6 of Chapter XX.

15. The catalyst tubes of problem 13 are surrounded by circulating flue gas which may be assumed to maintain the tube walls at a temperature of 1100°F. By a stepwise graphical integration establish the radial and longitudinal temperature and conversion distributions throughout the bed. Also calculate the average product distribution and pressure in the fluid stream as a function of longitudinal position, assuming uniform flow distribution. The effective thermal conductivity of the bed may be taken as 0.9.

16. It is proposed to place the catalyst of problem 7 in an envelope type of heat exchanger so arranged that the catalyst is in the form of vertical flat slabs 1 in. in thickness. The retaining walls are maintained at 1075°F, the temperature of the entering butane, by a circulating fluid. Using the space velocity and bed depth finally determined in problem 7, calculate by a stepwise integration the lateral and longitudinal distribution of temperature and conversion. Also calculate the longitudinal variation of the average conversion and product distribution of the fluid stream. The effective thermal conductivity of the bed may be taken as 0.9.

CHAPTER XXII

UNCATALYZED HETEROGENEOUS REACTIONS

Many of the catalytic reactions discussed in Chapter XIX are properly classified as heterogeneous, because more than one phase participates. However, in such catalytic reactions the initial reactants and final products are present in a single phase, and the net result is the same as though a homogeneous reaction had occurred. Uncatalyzed heterogeneous reactions are characterized by the presence of initial reactants or final products in more than one phase. Such a reacting system may include a gas phase and several distinct liquid or solid phases. For example, in the blast furnace, there may be present in one zone a system of gas, molten metal, molten slag, solid carbon, and several solid oxides, all participating in a complex series of reactions.

Many organic processes involve heterogeneous reactions of various types. The nitration and sulfonation of hydrocarbons are frequently carried out in liquid systems comprising two phases, one of which is predominantly acid and the other organic. The reaction products may be distributed between both phases. Alternately, these same reactions may be carried out in a homogeneous vapor phase or in a two-phase liquid and vapor system. The principles governing a reaction vary widely with the conditions under which it is conducted, and there is little logic in designating such a process as a " unit " for study on the basis of its reactants or products.

It is evident from the variety of types of heterogeneous reactions that many different mechanisms are possible. The actual reaction may occur in a homogeneous phase, on a solid surface, or at an interface separating two liquid phases or a gas and a liquid phase. In any case, however, a problem of mass transfer of reacting materials from one phase to another phase or to an interface is involved. The rates of these mass-transfer steps are governed by the principles discussed in Chapter XX. The net rate of reaction is then determined by the rate of the chemical change itself, by the rates of mass transfer, and in some cases by rates of adsorption on solid surfaces. Thus, as in the case of heterogeneous catalytic reactions, the rate is controlled by a series of steps, each of which may be considered as offering resistance to the progress resulting from the existing driving forces.

Two-phase uncatalyzed reactions are conveniently grouped in the following classifications:

1. Gas–liquid reactions typified by gas-absorption operations in which chemical change occurs. The absorption of carbon dioxide gas in caustic solution is an example.

2. Liquid–liquid reactions such as the nitration of toluene with mixed acid.

3. Gas–solid reactions in which either all products or all reactants are gaseous. The oxidation of carbon is an example.

4. Liquid–solid reactions in which either all products or all reactants are liquid as in the reaction of lime with hydrochloric acid.

If more than two phases are present many additional types of reactions are possible, of which the following are of particular interest:

5. Reacting systems composed of a gas and two solid phases. The low-temperature reduction of iron oxide with hydrogen or the absorption of CO_2 by lime are examples.

6. Reactions involving two liquid phases and a gas phase, as, for example, when nitric acid reacts with mercury with evolution of gases.

7. Solid–solid reactions typified by the sintering of powders. Some compounds have been produced only by this type of reaction.

Many other classifications could be cited, each of which would involve different combinations of the fundamental principles governing process behavior. However, for any one classification these principles should apply in a similar fashion, regardless of the particular compounds under consideration. For this reason it is believed desirable to study process problems from the viewpoint of " unit principles " rather than " unit processes " grouped together on the basis of similar chemistry.

Unfortunately at present there are sufficient data to permit sound kinetic analyses of only a few reaction types. Rate measurements are badly needed on other typical systems in order to segregate and evaluate the individual controlling principles. Of the seven types of reactions listed here, data are available only for the partial analysis of systems illustrating types 1, 2, and 3. Of these, type 1 is extensively treated in the standard texts on unit operations and gas absorption. No satisfactory fundamental method has been developed for problems involving chemical reaction in absorption, and at present such processes are designed from empirical over-all transfer coefficients. More data are needed on which to base a sound analysis of such problems.

LIQUID–LIQUID REACTIONS

Reactions between two relatively immiscible liquids are favored by intimate intermixing to produce a highly extended interfacial area in the nature of an emulsion and to approach an equilibrium distribution of all components in the two phases. With such intermingling the over-all reaction rate is influenced by the rates of diffusion to the interface, reaction at the interface, and homogeneous reactions in the two separate phases. The resistance to diffusion can be made negligible by effective agitation which results in a very large interfacial area per unit volume. Where two reactants are completely immiscible the chemical reaction step may be confined to the interface; as mutual solubility is increased the chemical steps become progressively more prominent in one or both of the separate phases.

Homogeneous Reaction in Separate Phases. In a frequently encountered liquid–liquid reaction, component A, which is highly soluble in phase a, reacts with component B, which is highly soluble in phase b. The two phases are of limited miscibility, and product R is highly soluble in phase a while product S is a highly soluble in phase b. The reaction may occur by a homogeneous mechanism in both phases. Equilibrium distribution of all components in both phases may be accomplished by effective agitation. For the general reaction $A + B \rightleftarrows R + S$, the rate in each phase is expressed by the following equations if a simple second-order mechanism is followed:

$$\text{Phase } a\text{:}\quad r_a = k_a\left(a_{Aa}a_{Ba} - \frac{a_{Ra}a_{Sa}}{K_a}\right) \tag{1}$$

$$\text{Phase } b\text{:}\quad r_b = k_b\left(a_{Ab}a_{Bb} - \frac{a_{Rb}a_{Sb}}{K_b}\right) \tag{2}$$

where a = activity
r = moles of A transformed per unit time per unit volume of an individual phase
k = reaction velocity constant
K = reaction equilibrium constant
Subscripts A, B, R, S refer to components A, B, R, and S
Subscripts a, b refer to phases a and b, respectively

If the agitation of the system is sufficient to maintain equilibrium distribution, the activity of each component in the phase in which it is less soluble may be expressed in terms of its activity in the phase in which it is more soluble. Thus, if R is more soluble in the a phase and S more soluble in the b phase,

$$\left.\begin{aligned} a_{Ab} &= K_A a_{Aa}; \qquad & a_{Ba} &= K_B a_{Bb} \\ a_{Rb} &= K_R a_{Ra}; \qquad & a_{Sa} &= K_S a_{Sb} \end{aligned}\right\} \tag{3}$$

where K_A, K_B, $\cdots$ = distribution equilibrium constants of A, B, etc. Equation (3) may be substituted in (1) and (2) and each activity expressed as the product of the mole fraction and the corresponding activity coefficient.

$$r_a = k_a \left(x_{Aa}\gamma_{Aa}x_{Bb}\gamma_{Bb}K_B - \frac{x_{Ra}\gamma_{Ra}x_{Sb}\gamma_{Sb}K_S}{K_a} \right) \tag{4}$$

$$r_b = k_b \left(x_{Aa}\gamma_{Aa}x_{Bb}\gamma_{B}K_A - \frac{x_{Ra}\gamma_{Ra}x_{Sb}\gamma_{Sb}K_R}{K_b} \right) \tag{5}$$

The over-all rate of reaction is the sum of the reactions in the two phases. Thus,

$$r = x_{Aa}\gamma_{Aa}x_{Bb}\gamma_{Bb}(V_ak_aK_B + V_bk_bK_A) - x_{Ra}\gamma_{Ra}x_{Sb}\gamma_{Sb}\left(\frac{V_ak_aK_S}{K_a} + \frac{V_bk_bK_R}{K_b} \right) \tag{6}$$

where r = rate of reaction of A, moles per unit volume of total system per unit time

V_a, V_b = fractional volumes of a and b phases, respectively

Thus,

$$V_a + V_b = 1.0$$

Application of Equation (6) is complicated by the extreme variations of the activity coefficients in liquid systems. In the general case it is necessary to express empirically each activity coefficient as a function of the composition of the phase to which it applies. Fortunately, in many systems some of these variations are negligible, and approximate methods may be used for the expression of others. A large over-all reaction equilibrium constant K_a or K_b simplifies the equation by eliminating the terms representing the reverse reaction. It is also common for the rate of reaction in one phase to be negligible in comparison to that in the other.

Illustration 1. Nitration of Aromatics. The nitration of aromatic hydrocarbons such as benzene, toluene, and xylene is an important heterogeneous liquid-phase reaction which has been extensively investigated. The process has been carried out for the most part in batch-type reactors equipped with agitators and cooling surfaces. The acid employed in such operations is a concentrated mixture of nitric and sulfuric acids containing 30–40 mole per cent H_2SO_4 and 10–30 mole per cent H_2O. It is generally considered that the function of the sulfuric acid is to maintain the nitric acid in a " dehydrated " state as a result of its strong affinity for water. If the nitration is carried out with strong nitric acid alone the rate of reaction is rapid at the start but drops off quickly as the water formed by the reaction dilutes the acid. This reduction in rate as the reaction proceeds is greatly lessened by the presence of sulfuric acid or some other " dehydrator."

Rates of mononitration when mixed nitric and sulfuric acid are employed have been measured by Lewis and Suen[1] on benzene and by McKinley and White[2] on toluene. Both groups of investigators made measurements in continuous equipment under steady-state conditions with high degrees of agitation to insure distribution equilibrium.

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[1] W. K. Lewis and T. J. Suen, *Ind. Eng. Chem.*, **32**, 1095 (1940).

[2] C. McKinley and R. R. White, *Trans. Am. Inst. Chem. Engrs.*, **40**, 143 (1944).

Thermodynamic and experimental data indicate that the equilibrium constant is very large for the nitration of aromatics under liquid-phase conditions. Accordingly, the reverse reaction may be neglected and the rate equation (6) written as follows if it is assumed that agitation is sufficient to approximate equilibrium distribution between the phases:

$$r = kx_{Aa}\gamma_{Aa}x_{Bb}\gamma_{Bb}(V_a + V_bK') \tag{7}$$

where $k = k_aK_B$
$K' = k_bK_A/k_aK_B$
x_{Aa} = mole fraction of HNO_3 in acid phase
x_{Bb} = mole fraction of aromatic in organic phase

The over-all reaction velocity constant k is a function of temperature which may be expressed by the Arrhenius equation.

$$\ln k = -\frac{E}{RT} + A \tag{8}$$

In applying Equation (7) the mutual solubility of the phases may be neglected and x_{Aa} based on the total HNO_3, H_2SO_4, and H_2O content of the system while x_{Bb} is based on the total benzene plus nitrobenzene.

The data of McKinley and White indicate that for the mononitration of toluene the activity coefficient of the toluene γ_{Bb} may be taken as unity over a wide range of conditions. It was also found that $K' = 0$, indicating that the reaction taking place in the organic phase is negligible. With these terms evaluated, rate data at a constant temperature may be used for empirical evaluation of the relative activity cofficients of the nitric acid γ_{Aa}.

The measurements of Lewis and Suen on the mononitration of benzene indicate that the activity coefficient of the benzene γ_{Bb} is increased by increased concentration of both nitrobenzene in the organic phase and nitric acid in the acid phase. An independent analysis of these data indicates that they are approximately represented by the following empirical expression for γ_{Bb} over a range of nitric acid concentrations from 2 to 10 mole per cent.

$$\gamma_{Bb} = 1 + 62x_{Aa}x_{Sb}{}^{(1+40x_{Aa})} \tag{9}$$

where x_{Sb} = mole fraction of nitrobenzene in the organic phase
x_{Aa} = mole fraction of nitric acid in the acid phase

Equation (9) is of uncertain accuracy for high nitric acid concentrations.

Values of γ_{Aa}, the relative activity coefficient of the nitric acid in the acid phase, were evaluated from the measurements of both groups of investigators[1, 2] and are plotted as a function of the acid-phase composition in Fig. 210. An arbitrary numerical scale has been assigned to these values. It should be noted that these coefficients express the activity of the particular form of nitric acid which is effective in the nitration reaction. This active form of nitric acid is believed to be a " dehydrated " or " pseudo " nitric acid, and the activity coefficients of this material do not necessarily bear any simple relationship to activity coefficients of HNO_3 as calculated from vapor pressure measurements by the methods of Chapter XIV. Great reliance should not be placed on the data of Fig. 210 in the regions where the broken lines indicate extrapolation of the experimental data.

With the assumption that the relative activity coefficients of Fig. 210 are independent of temperature, the other constants of Equations (7) and (8) for the mononitration of benzene and toluene in the temperature range from 15 to 50°C are as follows:

	Benzene	*Toluene*
γ_{Eb}	$1 + 62x_{Aa}(x_{Sb})^{(1+40x_{Aa})}$	1.0
K'	0.14	0
E cal per g-mole	14,000	14,000
A (rates in g-moles per hr per liter of combined phases)	26.22	27.58

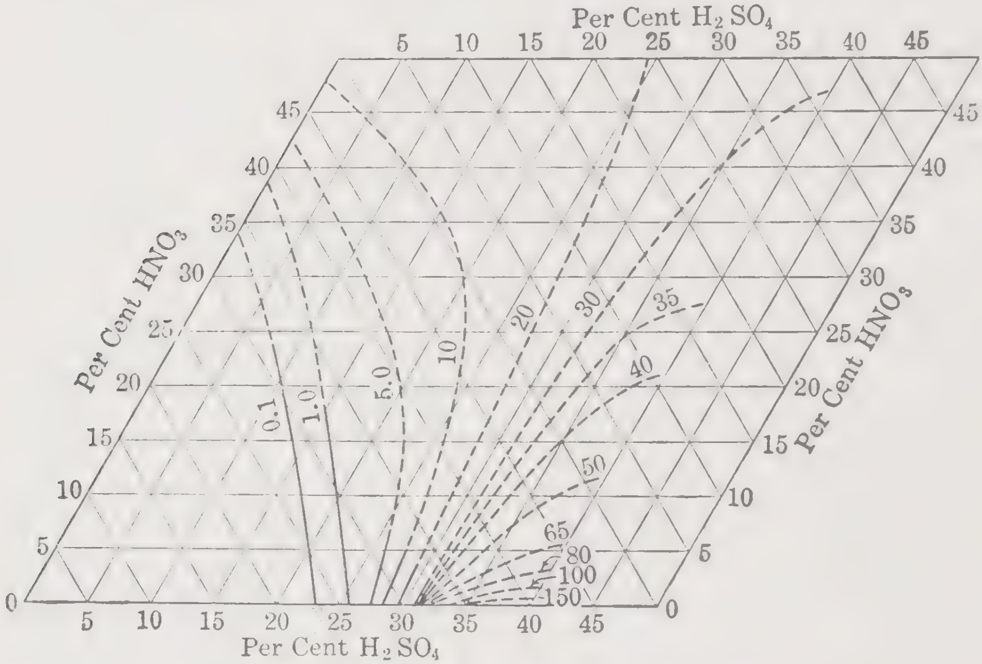


FIG. 210. Activity Coefficients of Mixed Acids.

As previously pointed out, these data are uncertain because of the limited ranges covered experimentally. If they are assumed to be correct the rates of processing under various conditions may be mathematically evaluated and compared to determine the optimum procedure where distribution equilibrium is maintained. This procedure is illustrated by the following problem.

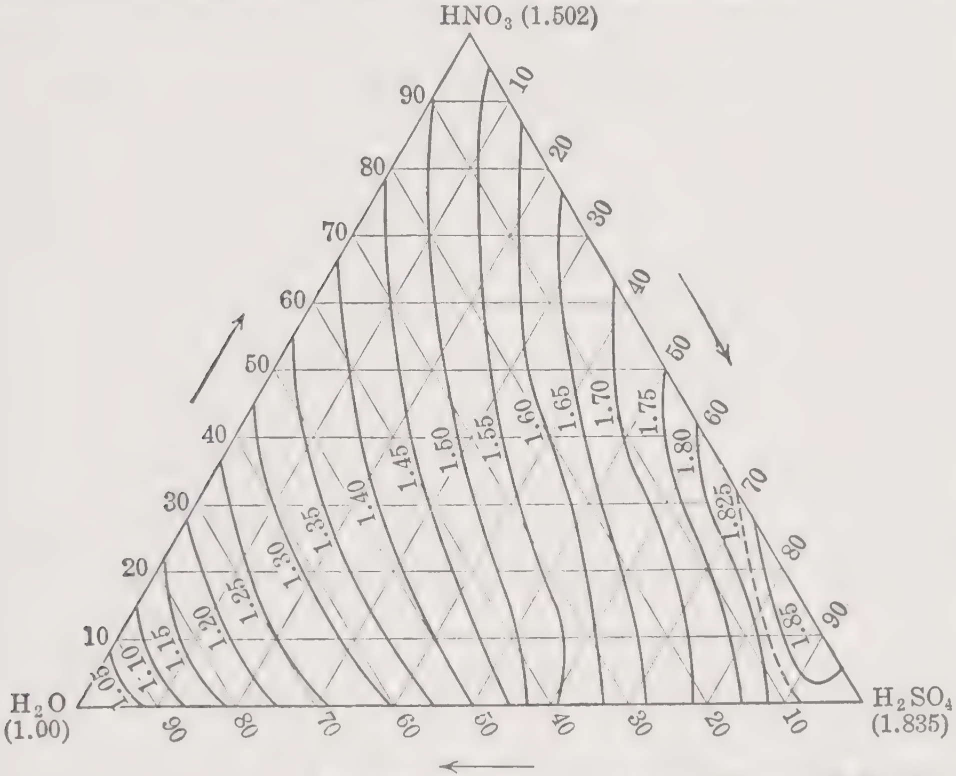
It is desired to produce 10,000 lb per day of mononitrobenzene by nitration of benzene with mixed acid. In a batch operation a mixed acid of the following composition is prepared by mixing cycle acid from a previous run with fresh acid:

	Mole Per Cent	*Weight Per Cent*
HNO_3	33.0	32.53
H_2SO_4	39.0	59.61
H_2O	28.0	7.86
	100.0	100.0

This acid is mixed with benzene to provide 2.5 per cent excess HNO_3 above that required to complete the formation of nitrobenzene. The densities of mixed nitrating acids are plotted in Fig. 211.

(*a*) Assuming that the acid and benzene are mixed together and maintained with adequate agitation at 35°C, calculate the minimum time required to obtain 99.5 per cent conversion to nitrobenzene.

(*b*) Calculate the volume of the reactor required for a capacity of 10,000 lb per day of nitrobenzene, allowing 2 hr for charging and discharging the reactor.



From Pascel and Garnier, *Bull. de la Societé Chemique*, **25**, 145 (1919).

FIG. 211. Densities of Mixed Acids at 18°C. Compositions are given in per cent by weight.

(Reproduced in "C.P.P. Charts")

(*c*) Calculate the volume required in a single-stage continuous reactor designed to produce the same conversion of benzene and the same waste acid composition as in parts (*a*) and (*b*). It may be assumed that sufficient agitation is provided to insure distribution equilibrium.

From the definition of reaction rate in a batch process

$$V_T = -\int \frac{dn_B}{r} \tag{10}$$

where n_B = moles of benzene per unit mass of original feed
V = total volume of mixture

The solution of Equation (10) requires a graphical integration with the aid of Figs. 210 and 211. For progressive conversion the changing compositions of the acid and benzene phases are calculated from a material balance, as summarized in Table A.

The corresponding values of γ_{Aa} are obtained from Fig. 210. Values of γ_{Bb} are calculated from Equation (9). Reaction rates r are then obtained by substitution in Equation (7) with the assumption that the term $(V_a + V_bK')$ is constant at the arithmetic average of the initial and final values. This assumption neglects the small variations in volume accompanying the reaction as a result of changes in densities or miscibility. Sample calculations of the initial and final rates are as follows:

Basis: 100 g-moles benzene charged requires 100 g-moles HNO_3 or 6320 g

$$HNO_3 \text{ charged} = 1.025(6320) = 6478 \text{ g}$$

$$\text{Weight of mixed acid} = \frac{6478}{0.3253} = 19{,}948 \text{ g}$$

$$\text{From Fig. 211, density} = 1.75$$

$$\text{Acid volume} = \frac{19{,}900}{1750} = 11.39 \text{ liters}$$

$$\text{Density of benzene} = 0.879$$

$$\text{Volume of benzene} = \frac{7800}{879} = 8.87 \text{ liters}$$

$$\text{Total initial volume} = 11.39 + 8.87 = 20.26 \text{ liters}$$

$$V_a = \frac{11.39}{20.26} = 0.562$$

$$V_b = 0.438$$

$$\text{Initially } k(V_a + K'V_b) = 29.08[0.562 + 0.14(0.438)] = 18.13$$

As the reaction proceeds the nitrobenzene formed dissolves in the benzene phase and is but slightly soluble in the acid phase at 99.5 per cent conversion.

$$V_b = \text{volume of benzene} + \text{volume of nitrobenzene}$$

$$V_b = \frac{(0.005)(7800)}{879} + \frac{(12{,}300)(0.995)}{1203} = 10.17 \text{ liters}$$

In acid phase:

$$\begin{array}{llrr}
H_2SO_4 & = (19{,}948)(0.596) & = 11{,}900 \text{ g} & 77.05\% \text{ wt} \\
HNO_3 & = 6478 - (99.5)(63.2) & = 190 \text{ g} & 1.23 \\
H_2O & = (19{,}948)(0.0786) + 99.5(18) & = \underline{3{,}358 \text{ g}} & \underline{21.72} \\
 & & 15{,}448 \text{ g} & 100.00
\end{array}$$

From Figure 211,

$$\text{Density of acid} = 1.695$$

$$\text{Acid volume} = \frac{15448}{1695} = 9.11 \text{ liters}$$

$$V = 9.11 + 10.17 = 19.28 \text{ liters}$$

$$V_a = \frac{9.11}{19.28} = 0.473$$

$$V_b = 0.527$$

$$k(V_a + K'V_b) = 29.08[0.473 + 0.14(0.527)] = 15.90$$

$$\text{Avg } k(V_a + K'V_b) = \frac{18.13 + 15.90}{2} = 17.01$$

The reaction rates are calculated by substituting this average value of $k(V_a + K'V_b)$ in Equation (7).

Initially $x_{Bb} = 1.0$; $x_{Aa} = 0.33$; $x_{Sb} = 0$
From Fig. 210, since the mole fraction of H_2SO_4 is 0.39, $\gamma_{Aa} = 33$
From Equation (9), $\gamma_{Bb} = 1 + (62)(0.33)(0)^{1+(40)(0.33)} = 1.0$
From Equation (7), $r = (17.01)(0.33)(33)(1)(1) = 185.3$
Finally, $x_{Bb} = 0.005$; $x_{Aa} = 0.0097$; $x_{Sb} = 0.995$
From Fig. 210, corresponding to 39 mole per cent H_2SO_4, $\gamma_{Aa} = 140$
From Equation (9), $\gamma_{Bb} = 1.0 + (62)(0.0097)(0.995)^{1+(40)(0.0097)} = 1.60$
From (7), $r = (17.01)(0.0097)(140)(0.005)(1.60) = 0.184$

TABLE A

NITRATION OF BENZENE

Basis: 100 g-moles benzene
r = (g-moles benzene)/(liter)(hr)

Per Cent Converted $100x_{Sb}$	x_{Bb}	x_{Aa}	γ_{Aa}	α $62x_{Aa}$	β $1 + 40x_{Aa}$	γ_{Bb} $1 + \alpha(x_{Sb})^\beta$	r	$1/r$
0	1.0	0.33	33	20.46	14.20	1.0	185.3	0.0054
5	0.95	0.3139	33.5	19.46	13.56		170	0.00588
10	0.90	0.2978	34	18.46	12.91		155	0.00645
15	0.85	0.2817	34.5	17.47	12.27		140.5	0.00711
20	0.80	0.2656	35.5	16.47	11.62		128.5	0.00778
25	0.75	0.2495	37	15.47	10.98		118	0.00848
30	0.70	0.2334	38.5	14.47	10.34		107	0.00935
35	0.65	0.2173	39.5	13.47	9.69	1.0	94.9	0.01054
40	0.60	0.2012	40.1	12.47	9.05	1.003	82.4	0.01213
45	0.55	0.1851	41.5	11.48	8.40	1.017	73.0	0.01370
50	0.50	0.1690	42.8	10.48	7.76	1.048	61.5	0.01626
55	0.45	0.1529	44.4	9.48	7.12	1.135	59.0	0.01695
60	0.40	0.1368	47	8.48	6.47	1.311	57.4	0.01742
65	0.35	0.1207	49	7.48	5.83	1.607	56.5	0.01770
70	0.30	0.1046	51	6.49	5.18	2.02	55.0	0.01816
75	0.25	0.0885	56	5.49	4.54	2.49	52.5	0.01904
80	0.20	0.0724	57	4.49	3.90	2.88	40.4	0.0248
85	0.15	0.0563	64	3.49	3.25	3.06	28.1	0.0356
90	0.10	0.0402	72	2.49	2.61	2.89	14.25	0.0702
95	0.05	0.0241	86	1.49	1.96	2.35	4.15	0.241
96	0.04	0.0209	90.5	1.30	1.84	2.21	2.84	0.352
97	0.03	0.0177	96	1.10	1.71	2.04	1.77	0.565
98	0.02	0.0145	110	0.90	1.58	1.872	1.016	0.985
99	0.01	0.0113	120	0.70	1.45	1.690	0.389	2.57
99.1	0.009	0.01094	125	0.678	1.438	1.669	0.35	2.86
99.2	0.008	0.0106	128	0.657	1.424	1.65	0.305	3.28
99.3	0.007	0.0103	132	0.639	1.412	1.633	0.265	3.77
99.4	0.006	0.0100	138	0.620	1.400	1.614	0.227	4.41
99.5	0.005	0.0097	140	0.601	1.388	1.597	0.184	5.44

Similar calculations for intermediate conversions are summarized in Table A. The resulting values of $1/r$ are plotted in Fig. 212 against $100x_{Bb}$, the moles of unconverted benzene left at any time. Because of the wide range of the variables the curve is plotted in three sections. The sum of the areas under these curves is the integral of Equation (10). Thus,

$$V\tau = 7.13 \quad \text{or} \quad \tau = (7.13)(60)/19.77 = 22.1 \text{ min}$$

(*b*) Total batch-reactor volume required to produce 10,000 lb of nitrobenzene per day, allowing 2 hr for filling and emptying.

Operating cycle = 2 + 22.1/60 = 2.368 hr
Charges per day = 24/2.368 = 10.1
Nitrobenzene per charge = 10,000/10.1 = 990 lb

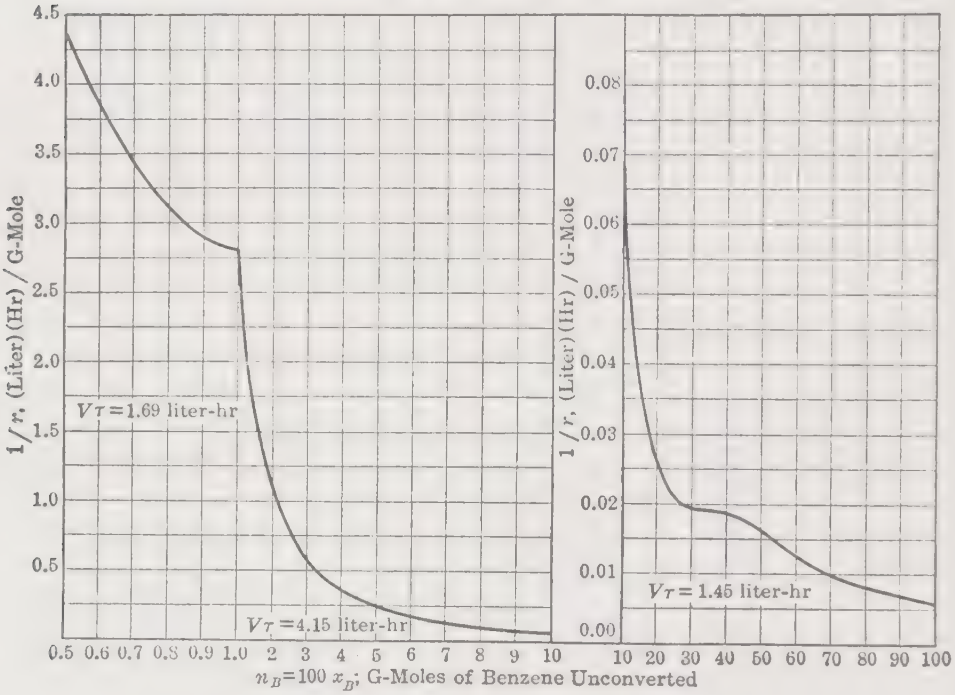


FIG. 212. Graphical Integration of $-\int_{n_{B0}}^{n_B} \frac{dn_B}{r}$

(Basis: 100 g-moles of benzene charged)

From part (a) an initial reactor volume of 20.26 liters is required for 12,240 g nitrobenzene

$$\text{Volume required} = \frac{(990)(454)(20.26)}{(12{,}240)(28.32)} = 26.3 \text{ cu ft}$$

(*c*) *Reactor Volume for Continuous Operation.* In a continuous operation the average conditions in the reactor are the same as those at the end of the batch operation. Under these conditions, from Table A, $r = 0.184$ g-moles/(liter)(hr) or (0.184)(28.32)/(454) = 0.01145 lb-moles/(cu ft)(hr).

Hourly production = (10,000)/(24)(123.1) = 3.38 lb-moles
Reactor volume = 3.38/0.01145 = 295 cu ft

Comparison of the results of parts (*b*) and (*c*) of Illustration 1 indicates that under the specified conditions the reactor volume required for continuous operation is over ten times that for the batch operation. However, the cost per unit volume of continuous reactor is relatively low because of the low maximum rate of release of heat of reaction. The cooling system for the batch reactor must be designed to handle the high rates of heat liberation at the start of the cycle where the reaction rate per unit volume is as much as 1000 times as great as in the continuous reactor. The continuous reactor thus has the advantage of permitting precise control of temperature with only a small fraction of the cooling surface required in the batch operation. In the actual operation of batch equipment of this type the high initial heat release is partially controlled by gradual addition of the reactants to retard the rate of reaction.

The large reactor volume required in a single-stage continuous operation may be avoided by using multiple stages in counterflow. In such an operation the hydrocarbon is charged to the first reactor where it is contacted with partially spent acid from the second reactor. The effluent from the first reactor is passed through a separator from which the waste acid is discarded and the hydrocarbon phase charged to the second contactor. The total reactor volume is progressively reduced by this type of multiple staging, and the optimum number of stages is determined by an economic analysis. A phase separator is required for each stage. A disadvantage of multiple-stage operation in the nitration of aromatics is an increased tendency toward secondary reactions forming di- and trinitro compounds.

Contactor Efficiency. Where agitation is not thorough, the distribution equilibria represented by Equation (3) may not be assumed. Thus, the actual activity of A in the b phase is less than the equilibrium value, $K_A a_{Aa}$ by an amount which is a function of the rate of reaction in the b phase, the over-all transfer coefficient of component A from the a to the b phase, and the extent of the interfacial area. Since relatively high concentrations of A and R exist in the a phase it may be assumed that the mass transfer of these components is controlled by a diffusional film at the interface in the b phase. Then

$$a_{Ab} = K_A a_{Aa} - \frac{r_b V_b}{k_A a_v} \tag{11}$$

where r_b = molal rate of reaction of A per unit volume of b phase
V_b = fractional volume of b phase
k_A = mass-transfer coefficient of A, moles per unit time per unit activity difference per unit interfacial area
a_v = interfacial area per unit of total volume

An expression similar to Equation (11) may be written for a_{Rb} and substituted in Equation (5).

$$r_b = k_b\left[\left(K_A a_{Aa} - \frac{r_b V_b}{k_A a_v}\right) a_{Bb} - \left(K_R a_{Ra} + \frac{r_b V_b}{k_R a_v}\right)\left(\frac{a_{Sb}}{K_b}\right)\right] \tag{12}$$

or

$$r_b\left[1 + \frac{k_b a_{Bb} V_b}{k_A a_v} + \frac{k_b a_{Sb} V_b}{k_R a_v K_b}\right] = k_b\left(K_A a_{Aa} a_{Bb} - \frac{K_R a_{Ra} a_{Sb}}{K_b}\right) \tag{13}$$

It may be noted that the right-hand side of Equation (13) is the same as that of Equation (2). Accordingly, the rate of reaction in this phase may be written as

$$r_b = E_{cb} k_b\left(a_{Aa} a_{Bb} K_A - \frac{a_{Ra} a_{Sb} K_R}{K_b}\right) \tag{14}$$

where E_{cb} is the *contactor efficiency* for the b-phase reaction defined as follows:

$$E_{cb} = \frac{1}{1 + \left(\dfrac{a_{Bb}}{k_A} + \dfrac{a_{Sb}}{k_R K_b}\right)\left(\dfrac{k_b V_b}{a_v}\right)} \tag{15}$$

A similar expression may be written for the contactor efficiency for the a-phase reaction. The contactor efficiency is increased by improved agitation which increases the transfer coefficients and interfacial area and is reduced by an increase in the reaction velocity constant or increases in the activities of the nondiffusing reactants or products. For the empirical evaluation of the contactor efficiency it is convenient to write Equation (15) in terms of diffusion film thickness ϕ_b and diffusion coefficients D_{Am} and D_{Rm}. Thus, since, in accordance with Equation (XX-26), page 981,

$$r_A = D_{Am}\frac{(a_A - a_{Ai})}{\phi_b} = k_A\,(a_A - a_{Ai}),$$

it follows that

$$k_A = \frac{D_{Am}}{\phi_b}$$

and

$$E_{cb} = \frac{1}{1 + \left(\dfrac{a_{Bb}}{D_{Am}} + \dfrac{a_{Sb}}{D_{Rm} K_b}\right)\dfrac{\phi_b}{a_v} k_b V_b} \tag{16}$$

where

D_{Am}, D_{Rm} = over-all diffusion coefficients of A and R from phase a to b
ϕ_b = effective diffusional film thickness in phase b
a_v = interfacial area, per unit total volume

The reaction velocity constants and activity coefficients of Equation (16) may be evaluated from rate measurements under conditions of extreme agitation where $E_c = 1.0$. Then, if the relative values of the diffusion coefficients are estimated by the methods outlined in Chapter XX, the ratio ϕ_b/a_v may be evaluated as a function of the power expended in agitation from a series of rate measurements at varying degrees of agitation. If the rate of reaction is important in both phases such tests must be repeated with different phase ratios in order to determine independently the contactor efficiencies for the two phases.

GAS-SOLID REACTIONS

Reactions between a gas and a solid may form either a gaseous or a solid product or both. If a solid product is formed three phases participate in the reaction and the mechanism is somewhat uncertain, but probably involves the formation of an activated complex involving both solid phases at a point of mutual contact between all three phases.

If only gaseous products are formed at least three mechanisms are possible.

1. The solid may sublime and the actual reaction occur in the homogeneous vapor phase.

2. A sufficiently energized gaseous-reactant molecule reacts upon impact with an active center on the solid surface to form a chemisorbed product molecule which is then desorbed. Only one active center is involved in this reaction, and if more than one product gas is formed only one is chemisorbed while the others are evolved directly with the gas phase.

3. The reactant gas is chemisorbed on the solid surface and then reacts with an adjacent active center to form chemisorbed product molecules which are then desorbed. Two adjacent active centers are involved in this mechanism, and if two product molecules are formed each may be chemisorbed on a separate site.

Reactions with Gaseous Products. A common general case is represented by the following equation:

$$A(s) + B(g) \rightleftarrows R(g) + S(g) \tag{17}$$

Rate expressions which are developed for this general reaction are readily modified to apply to the less complicated cases where the two product molecules are alike or where only a single product molecule is formed.

Sublimation Mechanism. The sublimation mechanism is possible even though the vapor pressure of the solid is very low. In such a case the rate of reaction may be controlled either by the rate of the homogeneous reaction or by the rates of sublimation and condensation. If the rate of the homogeneous reaction is controlling and mass-transfer effects are not important, it may be assumed that the activity of the gasified solid is constant at the equilibrium value and the rate expressed by the equations of Chapter XVIII. In such a case the rate of reaction per unit mass of solid is independent of the surface area exposed and proportional to the volume of the gas phase.

If the rate of sublimation is controlling it may be assumed that chemical equilibrium is maintained in the vapor phase. The rate of the forward reaction per unit mass of solid is then expressed by

$$r = A_m(k_{SA} - k'_{SA}a_{Ai}) = A_m\left(k_{SA} - k'_{SA}\frac{a_{Ri}a_{Si}}{K_g a_{Bi}}\right) \tag{18}$$

where

A_m = interfacial area, per unit mass of solid
k_{SA}, k'_{SA} = velocity constants for the sublimation and condensation of A
a_{Ai}, a_{Bi} = activities in the gas phase at the interface of components A, B, etc.
K_g = gas-phase-reaction equilibrium constant

When equilibrium is reached between the solid and gas phases,

$$(a_{Ai})_e = \frac{k_{SA}}{k'_{SA}} = K_{SA} \tag{19}$$

where K_{SA} is the sublimation equilibrium constant of A which is equal to its vapor pressure where the ideal-gas law is applicable. Combining (18) and (19) gives

$$r = A_m k_{SA}\left(1 - \frac{a_{Ri}a_{Si}}{K_{SA}K_g a_{Bi}}\right) \tag{20}$$

Data are not available to establish whether or not the sublimation mechanism is followed in any of the industrially important reactions of this type. It is possible that carbon and hydrogen are formed from methane at high temperatures by the reverse of such a reaction, with the rate of the homogeneous reaction controlling at the lower temperatures and the rate of sublimation or condensation controlling at higher temperatures. In considering such reactions, it is important to recognize that the activity of a very small aggregation of a solid is higher than the normal value of an extended surface. For this reason a condition of high supersaturation may exist in the gas phase if no solid phase is initially present. Once condensation of the solid is initiated by the formation of condensed nucleii these small particles will grow as the reaction proceeds.

Absorption Mechanism. There is evidence that in many gas–solid reactions one or more of the gaseous components is chemisorbed on the solid surface and the reaction actually occurs on the surface. Thus the reaction of Equation (17) might proceed in the forward direction by chemisorption of B on the surface of A followed by reaction to form chemisorbed molecules of R and S which are then desorbed. Since the rates of such activated phenomena differ widely it is general for one step of a sequence of this type to be so slow that equilibrium may be assumed in the others. The rate of the reaction is then controlled by the slow step which may be any one of the four.

Where two adsorbed product molecules are formed it is probable that the forward reaction occurs by an adsorbed B molecule reacting with an adjacent vacant adsorption center of the solid reactant A. The reaction rate is then expressed by

$$r = A_m(kc'_Bc'_l - k'c'_Rc'_S) = A_mk\left(c'_Bc'_l - \frac{c'_Rc'_S}{K'}\right) \tag{21}$$

where

r = rate of reaction per unit mass of solid
A_m = interfacial area per unit mass of solid
c'_B, c'_R, c'_S = concentration of adsorbed B, R, S molecules per unit area
c'_l = concentration of vacant reaction sites per unit area
k, k' = velocity constants of forward and reverse surface reactions, respectively
K' = surface-reaction equilibrium constant = $c'_Rc'_S/c'_Bc'_l$

If the surface reaction is the slow rate-determining step surface concentrations in Equation (21) are the adsorption-equilibrium values expressed by Equations (XIX-10 and 11), page 911. Combining these equations yields

$$r = \frac{A_m(L')^2k}{(1 + a_{Bi}K_B + a_{Ri}K_R + a_{Si}K_S + a_{Ii}K_I)^2}\left(a_{Bi}K_B - \frac{a_{Ri}K_Ra_{Si}K_S}{K'}\right) \tag{22}$$

When equilibrium is reached,

$$\left(\frac{a_{Ri}a_{Si}}{a_{Bi}}\right) = \frac{K_B K'}{K_R K_S} = K \tag{23}$$

where K = the over-all thermodynamic equilibrium constant.

Combining (22) and (23) gives

$$r = \frac{A_m L'^2 K_B k}{(1 + a_{Bi}K_B + a_{Ri}K_R + a_{Si}K_S + a_{Ii}K_I)^2}\left(a_{Bi} - \frac{a_{Ri}a_{Si}}{K}\right) \tag{24}$$

where, K_B, K_R, etc. = adsorption-equilibrium constants.

It is evident from Equation (24) that where this mechanism is followed the rate is proportional to the interfacial area and to the number of active centers for reaction per unit area. The relationship with the activities of the gaseous reactants may be complex if the adsorption-equilibrium constants are large, corresponding to extensive coverage of the surface with adsorbed molecules. The rate may be diminished by increased activity of the reactant B if its adsorption-equilibrium constant is large.

If the adsorption of the reactant B is the rate-determining step the surface concentration of B is fixed by the equilibrium of the surface reaction and the other adsorptions. The rate of reaction is expressed by a combination of Equations (XIX-6 and 7), page 910.

$$r = A_m k_B\left(a_{Bi}c_l' - \frac{c_B'}{K_B}\right) \tag{25}$$

where k_B = adsorption velocity constant of B

K_B = adsorption-equilibrium constant of B

From the equilibria of the surface reaction and the adsorption of R and S:

$$c_B' = \frac{c_R'c_S'}{K'c_l'} = \frac{a_{Ri}c_l'K_R a_{Si}c_l'K_S}{K'c_l'} = \frac{a_{Ri}a_{Si}K_B c_l'}{K} \tag{26}$$

$$c_l' = L' - [c_B' + c_R' + c_S' + c_I'] \tag{27}$$

Combining (26) and (27) results in

$$c_l' = \frac{L'}{1 + \dfrac{a_{Ri}a_{Si}K_B}{K} + a_{Ri}K_R + a_{Si}K_S + a_{Ii}K_I} \tag{28}$$

Substituting (28) and (26) in (25) gives

$$r = \frac{A_m k_B L'}{\left(1 + \frac{a_{Ri} a_{Si} K_B}{K} + a_{Ri} K_R + a_{Si} K_S + a_{Ii} K_I\right)} \left(a_{Bi} - \frac{a_{Ri} a_{Si}}{K}\right) \qquad (29)$$

It may be noted that a_{Bi}, the activity of B at the interface, appears only once in Equation (29). Where this mechanism is followed the rate is increased over the entire range by increased activity of the gaseous reactant B.

If two like product molecules R are formed in the reaction, Equations (24) and (29) are modified by omitting the term $a_{Si}K_S$ and replacing $a_{Ri}a_{Si}$ by $(a_{Ri})^2$. If only a single product molecule R is formed all terms pertaining to component S are omitted.

It is evident that where chemisorption is involved in uncatalyzed heterogeneous reactions the rate equations are of the same general forms as those developed in Chapter XIX. By these same methods rate equations are readily derived for cases where the rate-controlling step is the desorption of a product gas or where dissociation of one of the reactant or product gases is involved. Similar equations may be derived for the case where reaction occurs between a gas-phase molecule and a single active center.

As in the case of catalytic reactions the proper mechanism and the rate-determining step can be identified only by the analysis of rate measurements over a sufficient range of conditions to test the applicability of the various equations. With such data available many of the possible rate equations may be eliminated merely by comparison of the trends of the data with those of the equations. The final determination frequently requires the evaluation of the constants in two or more equations in order to determine which properly represents the data.

The constants of these rate equations can only be evaluated empirically from rate measurements, and it has not been proved feasible to employ adsorption-equilibrium constants determined by adsorption measurements made on individual components. However, such adsorption measurements may serve to indicate that some of the equilibrium constants are negligible.

The similarity between rate equations for gas–solid reactions and gas reactions catalyzed by solids is apparent. The distinction becomes evident upon application where in the gas–solid reactions the solid disappears and the surface area per unit mass of solid changes as the reaction proceeds, whereas in catalytic reactions these quantities remain constant.

Mass-Transfer Effects. In the rate equations developed in the preceding section the activities are in all cases those existing at the interfaces. The interfacial activities of the gaseous components differ from the activities in the main gas stream as a result of the gradients required to cause diffusion to and from the interface. These activity differences may be calculated from the mass-transfer relationships developed in Chapter XX.

As in the case of catalytic reactions the importance of mass-transfer effects varies widely. In many systems where the chemical rates are low and mass velocities are high the mass-transfer resistances may be neglected. Since mass-transfer rates are little affected by temperature it is possible for the over-all rate of a reaction to be controlled entirely by chemical steps at low temperatures and by mass transfer at high temperatures where the chemical rates are relatively high. In such a case the temperature coefficient of the over-all reaction rate diminishes as temperature is increased, and where mass-transfer resistances are dominant, temperature has little effect on rate of reaction.

Illustration 2. Extensive tests on the combustion in air of coke on grates[3] indicate that at the high temperatures encountered the rate of the reaction is primarily limited by mass transfer. Although the experimental errors in the work were large, the data obtained are in general consistent with the following mechanism:

1. Oxygen diffuses from the air stream to the surface of the coke particle where it reacts to form CO or CO_2. It may be assumed that at the high temperatures involved the chemical reactions on the surface are so fast that chemical equilibrium is maintained among C, CO, CO_2, and O_2. Reference to Fig. 156, page 712, shows that at temperatures above 1300°K the equilibrium concentrations of both CO_2 and O_2 are substantially zero.

2. Carbon monoxide diffuses from the interface into the gas stream where if oxygen is present it is oxidized to carbon dioxide in a homogeneous gas-phase reaction:

$$2CO + O_2 \rightleftarrows 2CO_2$$

3. As the carbon dioxide content of the gas stream is built up by steps 1 and 2, CO_2 diffuses to the interface where it is reduced to CO in a surface reaction:

$$CO_2(g) + C(s) \rightleftarrows 2CO$$

In a deep fuel bed this reaction continues after all oxygen is consumed, and the final products approach an equilibrium composition containing substantially no CO_2.

On the basis of the assumption of equilibrium at the high-temperature interface, the rates of steps 1 and 3 are controlled entirely by diffusion and may be calculated from the data of Fig. 194. Step 2 is a homogeneous reaction which has been studied by Haslam[4] with the conclusion that it approximates a third-order mechanism in accordance with the stoichiometric equation. Measurements of spontaneous ignition temperatures by Falk[5] indicate that the rate of reaction is increased by a factor of

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[3] Kreisinger, Ovitz, and Augustine, *U. S. Bur. Mines Tech. Paper* 137 (1916).

[4] R. T. Haslam, *Ind. Eng. Chem.*, **15**, 679 (1923).

[5] K. G. Falk, *J. Am. Chem., Soc.*, **29**, 1536 (1907).

1.14 as a result of a 10°C increase in temperature at 1000°C. This corresponds to an apparent energy of activation of approximately 42,000 cal/(g-mole)(°K). Since the equilibrium constant (Fig. 156) corresponds to a negligible reverse reaction at temperatures up to 2000°K the rate of this reaction may be expressed by the following equation,

$$r = k(p_{\mathrm{CO}})^2 p_{\mathrm{O_2}} \tag{30}$$

where

r = rate of consumption of oxygen based on gas-phase volume, lb-moles/(cu ft)(hr)

$p_{\mathrm{CO}}, p_{\mathrm{O_2}}$ = partial pressures of CO and O_2, respectively, atmospheres

Analysis of the data of Kreisinger, Ovitz and Augustine indicates that the reaction velocity constant k is expressed by the following equation, which includes the energy of activation derived from Falk's measurements,

$$\ln k = -\frac{42{,}000}{RT} + 24.74414$$

or

$$\log k = -\frac{9179.7}{T} + 10.7462 \tag{31}$$

where T = degrees Kelvin

Because of the experimental errors inherent in combustion measurements, the data of Kreisinger, Ovitz, and Augustine show inconsistencies when single runs are compared with each other. A better picture of the combustion process is obtained by considering the average results of a series of similar runs. In one series air was passed at rates varying from 380 to 756 lb/(sq ft) (hr). The average rate for the series was approximately 600 lb/(sq ft)(hr). The temperatures in the lower sections of the fuel beds averaged approximately 2600°F. In each test coke which was sized between 1½- and 1-in. screens was continuously fed to the top of the fuel bed, and the grates were kept clean and free from all but a thin layer of ash. On the basis of Equations (30) and (31) and the mass-transfer relationships of Chapter XX it is desired to calculate the composition of the gas phase throughout the fuel bed in this series of runs.

Solution: In order to calculate mass-transfer rates some assumptions are necessary regarding the particle sizes in the bed. Actually the particle size diminishes from a maximum at the top to a minimum at the bottom. However, as the size is reduced, the particle becomes coated with ash which increases the resistance to mass transfer, tending to offset the effect of reduced particle size. Accordingly, it will be assumed that the particle size is constant at the size of the coke fed. If it is assumed that the particles are approximately spherical and pack with a void space of 50 per cent, the superficial surface area a per cu ft of bed, is calculated as follows:

$$\text{Volume per particle} = \left(\frac{1.25}{12}\right)^3 \frac{\pi}{6} = (0.59)(10^{-3}) \text{ cu ft}$$

$$\text{Area per particle} = \left(\frac{1.25}{12}\right)^2 \pi = (3.4)(10^{-2}) \text{ sq ft}$$

$$\text{Area per cu ft} = \frac{(0.50)(3.4)(10^{-2})}{(0.59)(10^{-3})} = 28.8 \text{ sq ft per cu ft}$$

TABLE A—

Basis: 1 sq ft of grate area;
Oxygen entering = 4.35 lb-moles per hr;

Section, in. from grate	0–0.25	0–0.25	0.25–0.5	0.5–0.75
Volume, Δv, cu ft	0.0208	0.0208	0.0208	0.0208
Trial no.	1	2	1	1
Est. avg. partial pressure, atm.				
O_2	0.200	0.205	0.195	0.176
CO_2	0.007	0.001	0.007	0.021
CO	0.006	0.007	0.016	0.0195
Reaction rates, lb-mole/(hr)(cu ft)				
r_1	8.00	8.20	7.80	7.05
r_2	0.80	1.11	5.55	7.45
r_3	0.25	0.04	0.25	0.76
$r_1 + r_2$	8.80	9.31	13.35	14.50
$2r_2 - r_3$	1.35	2.18	10.85	14.14
$2(r_1 + r_3 - r_2)$	14.90	14.26	5.00	0.72
Incremental changes, lb-moles per hr				
ΔO_2	−0.183	−0.194	−0.278	−0.301
ΔCO_2	0.028	0.043	0.226	0.294
ΔCO	0.310	0.297	0.104	0.015
Gas leaving section, lb-moles per hr				
O_2	4.167	4.156	3.878	3.577
CO_2	0.028	0.043	0.269	0.563
CO	0.310	0.297	0.401	0.416
N_2	16.350	16.350	16.350	16.350
Total	20.855	20.846	20.898	20.906
Composition of gas leaving, mole per cent				
O_2	20.00	20.00	18.52	17.1
CO_2	0.13	0.20	1.29	2.69
CO	1.49	1.42	1.92	1.99

In view of the approximations required with respect to area, it is satisfactory to neglect variations in mass velocity, viscosity, density, and diffusion coefficients throughout the bed and assume constant average values.

$$\text{Mass velocity of air entering} = 600 \text{ lb}/(\text{hr})(\text{sq ft})$$

This mass velocity is 20.7 lb-moles/(hr)(sq ft), containing 4.35 lb-moles of oxygen.
Mass velocity of gas leaving with oxygen as CO $= 600 + (4.35)(24) = 704$
Average mass velocity $= 652$ lb/(hr)(sq ft)

$$\text{Average gas density, } \rho = \frac{652}{(20.7 + 2.17)(359)(3060/492)} = 0.0128 \text{ lb per cu ft}$$

Average molecular weight $= 652/22.87 = 28.5$

The average viscosity may be taken as approximately that of air which is given in the International Critical Tables as 358.3 micropoises at 500°C and atmospheric pressure. Based on the critical temperature of air as −140.7°C, its reduced tempera-

COMBUSTION OF COKE IN AIR

air rate = 600 lb/(hr)(sq ft);
N_2 entering = 16.35 lb-moles per hr

0.75–1.0	5.0–5.5	5.5–6.0	6.0–6.5	6.5–7.0	7.0–8.0	8.0–9.0	9–10
0.0208	0.0416	0.0416	0.0416	0.0416	0.0832	0.0832	0.0832
1	1	1	1	1	1	1	1
0.163	0.008	0.003	0.0013	......			
0.037	0.166	0.164	0.155	0.144	0.128	0.108	0.096
0.0205	0.059	0.070	0.089	0.110	0.140	0.166	0.184
6.53	0.32	0.12	0.05	....	....	....	....
7.60	3.09	1.63	1.14	....	....	....	....
1.34	6.02	5.95	5.61	5.21	4.65	3.90	3.46
14.13	3.41	1.83	1.19	....	....	....	....
13.86	0.16	−2.69	−3.33	−5.21	−4.65	−3.90	−3.46
0.54	6.50	8.88	9.04	10.42	9.30	7.80	6.92
−0.295	−0.142	−0.076	−0.050	....	....	....	....
0.291	0.006	−0.112	−0.138	−0.216	−0.386	−0.319	−0.282
0.011	0.270	0.370	0.375	0.435	0.772	0.637	0.565
3.282	0.122	0.046	−0.004	....	....	....	....
0.854	3.533	3.421	3.283	3.067	2.681	2.362	2.080
0.427	1.381	1.751	2.126	2.561	3.333	3.970	4.535
16.350	16.350	16.350	16.350	16.350	16.350	16.350	16.350
20.913	21.386	21.568	21.755	21.978	22.364	22.682	22.965
15.7	0.57	0.21	....	....	....	....	....
4.08	16.60	15.90	15.0	14.0	12.0	10.4	9.1
2.04	6.49	8.15	9.8	11.6	14.9	17.5	19.8

ture at 500°C is 5.85, whereas the bed temperature of 2600°F corresponds to a reduced temperature of 12.9. Extrapolating Fig. 175 yields

$$\text{Viscosity at } 2600°\text{F} = 358.3(2.9/1.8) = 577 \text{ micropoises}$$

or

$$(2.42)(10^{-4})(577) = 0.14 \text{ lb}/(\text{ft})(\text{hr})$$

The components whose diffusion limits the rate of combustion are O_2 and CO_2. Since nitrogen represents a large proportion of the gas stream, a good approximation may be obtained by assuming that these components are each diffusing in an atmosphere of nitrogen. On this basis the diffusion coefficients are calculated from Equation XX-50), page 988.

For oxygen, at 2600°F (1700°K):

$$D_v = \frac{(0.0043)(1700)^{\frac{3}{2}}}{[(25.6)^{\frac{1}{3}} + (31.2)^{\frac{1}{3}}]^2}\sqrt{\frac{1}{32} + \frac{1}{28}}$$

$$= 2.07 \text{ sq cm per sec or } (3.88)(2.07) = 8.02 \text{ sq ft per hr}$$

For CO_2:

$$D_v = \frac{(0.0043)(1700)^{\frac{3}{2}}}{[(34)^{\frac{1}{3}} + (31.2)^{\frac{1}{3}}]^2}\sqrt{\frac{1}{44} + \frac{1}{28}}$$

$$= 1.77 \text{ sq cm per sec or } (3.88)(1.77) = 6.9 \text{ sq ft per hr}$$

In order to obtain $a_v H_{dG}$ from Fig. 194, page 987, the dimensionless groups D_pG/μ and $\mu/\rho D_v$ must be evaluated. On the assumption of spherical particles, $D_p = 1.25/12 = 0.104$ ft.

$$\frac{D_pG}{\mu} = \frac{(0.104)(652)}{0.14} = 485$$

For O_2:

$$\frac{\mu}{\rho D_v} = \frac{0.14}{(0.0128)(8.02)} = 1.36$$

For CO_2:

$$\frac{\mu}{\rho D_v} = \frac{0.14}{(0.0128)(6.9)} = 1.58$$

From Fig. 194 or Equations (XX-39 and 44),

For O_2: $a_v H_{dG} = 15.7$; $H_{dG} = 15.7/28.8 = 0.545$ ft

For CO_2: $a_v H_{dG} = 17.3$; $H_{dG} = 17.3/28.8 = 0.600$ ft

The value of p_f for the diffusion may be calculated from Equation (XX-23), page 979. Since the variation of $(\pi + \delta p_A)$ is small the arithmetic mean may be used. It is assumed that p_A is zero at the interface for both O_2 and CO_2 while in the main gas stream it will vary from zero to 0.21. Since $\delta = 1.0$, p_f varies from 1.0 to 1.105. An average value of 1.05 may be used.

By substituting in Equation (XX-48), page 986, the rates of diffusion of O_2 and CO_2 are obtained on the basis of 1 cu ft of fuel bed.

For O_2 (step 1 of the combustion process):

$$r_1 = -\frac{\Delta pG}{M_m p_f H_{dG}} = \frac{652p_{O_2}}{(28.5)(1.05)(0.545)} = 40.0p_{O_2} \frac{\text{lb-moles } O_2}{(\text{cu ft})(\text{hr})}$$

For CO_2 (step 3 of the combustion process):

$$r_3 = \frac{652p_{CO_2}}{(28.5)(1.05)(0.600)} = 36.2p_{CO_2} \frac{\text{lb-moles } CO_2}{(\text{cu ft})(\text{hr})}$$

where the partial pressures are expressed in atmospheres.

The reaction velocity constant of the gas-phase oxidation of CO is given by Equation (31).

$$\log k = -\frac{9179.7}{1700} + 10.7462 = 5.3464$$

$$k = 0.222\ (10^6)$$

Since the bed is assumed to contain 50 per cent voids, the rate of step 2, the gas-phase reaction, per cubic foot of bed is given by the equation:

$$r_2 = 0.111\ (10)^6(p_{CO})^2(p_{O_2}) \frac{\text{lb-moles } O_2}{(\text{cu ft})(\text{hr})}$$

On the basis of the assumptions established these three rate equations may be applied to an incremental section of bed having a volume Δv to determine the rates of disappearance of O_2 and formation of CO and CO_2. Thus:

$$\text{Disappearance of oxygen} = -\Delta O_2 = (r_1 + r_2)\Delta v \text{ lb-moles per hr}$$

$$\text{Formation of } CO_2 = \Delta CO_2 = (2r_2 - r_3)\Delta v \text{ lb-moles per hr}$$

$$\text{Formation of } CO = \Delta CO = 2(r_1 + r_3 - r_2)\Delta v \text{ lb-moles per hr}$$

These three relationships may be applied successively to small increments of bed depth, starting from the grate and developing curves relating the composition of the gas stream to position in the fuel bed. The procedure is that of the typical stepwise integration in which the rates in each increment are based on arithmetic average partial pressures which are adjusted by successive approximations to correspond to the calculated composition changes. These calculations are shown in Table A for bed depths from 0 to 1.0 and from 5 to 10 in. The intervening calculations from 1 to 5 in. were carried out by the same procedure. The resulting curves for the percentages of O_2, CO_2, and CO are plotted as a function of bed depth in Fig. 213.

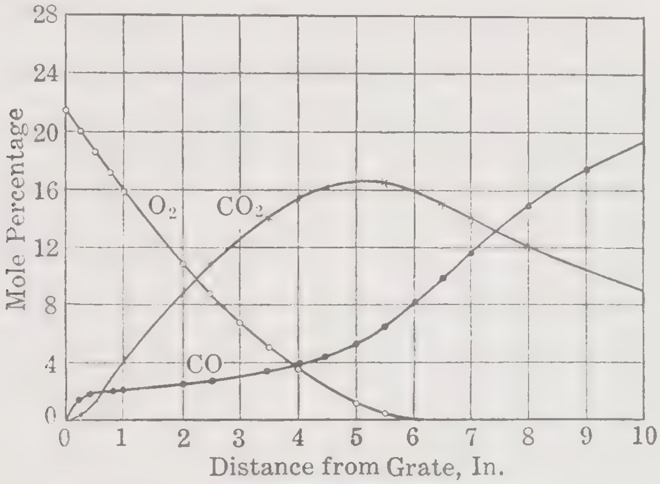

Fig. 213. Composition of Gas in the Combustion of Coke on a Grate.

Air rate = 600 lb/(sq ft)(hr)
Average temperature = 2600°F.

The curves of Fig. 213 are in fair agreement with the average experimental results[3] with the exception of the CO concentrations near the grate. The experimentally observed CO concentrations at a distance of 1.5 in. from the grate were slightly less than 1 per cent, whereas the calculated value at this point is 2.2 per cent. These low initial CO concentrations have been generally interpreted as indicating that the primary combustion reaction is the formation of CO_2 rather than CO at the surface. However, it is believed that the differences between the observed CO values and those calculated on the basis of the assumptions of Fig. 213 are within the probable error of the measurements. The problem of obtaining a representative sample of CO in the presence of a large excess of oxygen at high temperatures is extremely difficult and it would be expected that the CO concentrations would tend to be too low.

The assumption of chemical equilibrium at the interface in Illustration 2 would not be satisfactory at low temperatures or when dealing with a particularly unreactive type of coke. Under such conditions the rate of reduction of CO_2 would have a significant effect on the over-all rate, and it would be improper to assume an interfacial CO_2 concentration of zero. As a result, higher maximum CO_2 concentrations would be reached in the gas stream. It seems probable that the rate of combination of O_2 with carbon can be neglected over wide ranges of conditions, but under extreme conditions it would also have to be considered, with a finite O_2 concentration at the interface. In such cases calculations of rates and composition changes would require evaluation of rate equations for the interfacial reactions. The general procedure followed would be that developed in Chapter XIX for cases where both mass-transfer and surface-reaction rates are of importance.

LIQUID-SOLID REACTIONS

Many intermittent chemical reactions are carried out in granular beds where some component in the fluid phase reacts with a component in the solid phase and is held there until recovered or eliminated by regeneration of the solid. Such processes are intermittent, involving a progressive change with time in both solid and fluid at each cross section of the bed and requiring regeneration when the capacity of the solid for further reaction is exhausted or when the effluent fluid begins to show insufficient recovery or change. One of the most common and familiar examples of this type of process is in the softening of water by a granular bed of a cation exchanger. In addition to the removal of calcium and magnesium ions from water such exchangers have been developed for the removal of iron from water for textile mills, hydrogen from water for beverage purposes and in the recovery of nickel and copper from waste-refinery solutions. The gradual poisoning of a catalyst by adsorption of some impurity may be considered in this same category. A pattern for the mathematical treatment of the rate equations in this type of process cannot be prescribed. Unique treatment is required for each different case arising. Only in a few cases have successful mathematical devices been developed for solving the unique differential equations established. An illustration of this type of process is presented here for the removal of minerals from water by a granular cation exchanger.

Water Softening. The softening of water is accomplished by the removal of metallic ions from the water in exchange for sodium ions from the exchanger. The reverse reaction predominates in the regeneration of the spent exchanger with sodium salt solution. The most plausible theory of the rate of cation exchange consistent with experimental data is that the instantaneous rate of softening at constant temperature and constant flow rate is proportional to the product of the concentration of calcium ions in the water and the square of the concentration of available sodium in the exchanger. The rate equations consistent with this theory and experimental evidence are as follows:

$$\text{Forward reaction rate: } r_1 = \frac{\partial p}{\partial \tau} = k_1 u v^2 \tag{32}$$

$$\text{Reverse reaction rate: } r_2 = -\frac{\partial p}{\partial \tau} = k_2(\gamma q)^2 p \tag{33}$$

$$\text{Net reaction rate: } r_n = k_1 u v^2 - k_2(\gamma q)^2 p \tag{34}$$

where p = calcium content of exchanger in equivalents per unit mass
v = sodium content of exchanger in equivalents per unit mass
q = sodium content of water, equivalents per million parts by weight of water
u = calcium content of water, equivalents per million parts by weight of water
r_1 = equivalents of calcium removed by exchanger/(unit mass) (unit time)
r_2 = equivalents of calcium removed from exchanger/(unit mass) (unit time)
r_n = net rate of softening, equivalents/(unit mass) (unit time)
γ = activity coefficient for sodium ion in solution; at low concentration, $\gamma = 1$

Du Domaine, Swain, and Hougen[6] found that the reaction velocity constants in the units previously defined were independent of fluid velocity but increased with decreasing particle size of exchanger as follows:

Mesh Size	k_1
28–35	2.86
20–28	2.29
14–20	1.91
2–14	1.62

The equilibrium constant for the reaction, $K = k_1/k_2$ was found to be 241,000. In the softening period the reverse reaction was found to be negligible in a flow system where the water enters with no sodium content.

In the softening period the variables u, v, p, and q are functions of distance x and time τ. For an element of the bed, at depth x, dx in thickness and unit area in cross section normal to the direction of water flow, the following differential calcium balance can be set up for the interval of time $d\tau$.

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[6] J. Du Domaine, R. L. Swain and O. A. Hougen, *Ind. Eng. Chem.*, **35**, 546–54 (1943).

$$\frac{1}{10^6} G\, d\tau \left(-\frac{\partial u}{\partial x}\, dx \right) = \rho\, dx \left(\frac{\partial p}{\partial \tau}\, d\tau \right) + \frac{\rho_w V_f}{10^6} \frac{\partial u}{\partial \tau}\, dx\, d\tau \tag{35}$$

The last term in this equation represents the change in calcium content in the water in the free space of the bed which is negligible compared to the total amount of water passed through. Neglecting this term and simplifying gives

$$\frac{\partial u}{\partial x} = -\frac{10^6 \rho}{G} \frac{\partial p}{\partial \tau} \tag{36}$$

where ρ = mass of exchanger per unit total volume of bed, bulk density
ρ_w = density of water, mass per unit volume
G = mass velocity, mass per unit area per unit time
V_f = volume fraction of water space in bed

Since each gram equivalent of calcium ion added to the exchanger is replaced by one gram equivalent of sodium,

$$p - p_0 = v_0 - v \tag{37}$$

or

$$\frac{\partial v}{\partial \tau} = -\frac{\partial p}{\partial \tau} \tag{38}$$

Combining Equation (32) with (36) and (38) gives

$$\left.\begin{aligned} \frac{\partial u}{\partial x} &= auv^2 \\ \frac{\partial v}{\partial \tau} &= buv^2 \end{aligned}\right\} \tag{39}$$

where $a = -10^6 \dfrac{\rho k_1}{G}$ and $b = -k_1$

For the usual boundary conditions that the entering water has a constant composition with time, and that the initial composition of the exchanger is uniform, Swain[6] has developed the following solution to Equation (39):

$$\left.\begin{aligned} \ln z + z &= \ln s + s - r \\ \frac{v}{v_0} &= \frac{1}{1 + z} \\ \frac{u}{u_0} &= \frac{1 + \dfrac{1}{s}}{1 + \dfrac{1}{z}} \end{aligned}\right\} \tag{40}$$

where

$$\left.\begin{aligned} r &= -av_0^2x = \frac{10^6\rho k_1 v_0^2 x}{G} \\ s &= -bu_0v_0\tau = k_1u_0v_0\tau \\ z &= \frac{v_0}{v} - 1 \end{aligned}\right\} \qquad (41)$$

A detailed study of the application of these equations to water softening shows the surprising results that, when hard water which enters free of sodium flows through a bed of exchanger, the reverse rate is nearly negligible under condition of steady fluid flow, and the exchanger becomes completely spent before chemical equilibrium is attained.

To expedite calculations, performance charts have been constructed from Equation (40) expressing the effects of all variables in terms of the dimensionless groups, r, s, s/r and u/u_0.

In Fig. 214 u/u_0 is plotted against s/r for constant values of r. In Fig. 215, values of r are plotted against s for such conditions that the residual hardness of the water leaving the bed is seven parts of calcium carbonate per million parts of water.

Illustration 3. It is desired to estimate the residual hardness of water after steady operation of a softener for 16 hr, with water flowing through a bed 3 ft thick at a rate of 4 gal per sq ft per min. The initial hardness of the water corresponds to 300 parts calcium carbonate per million parts of water, which is equal to 6.0 lb equivalents of calcium ion per million lb of water. The initial replaceable sodium content of the exchanger is equivalent to 25,000 grains of calcium carbonate per cu ft. The density of the mineral is 28 lb per cu ft, and the grain size is 14 to 20 mesh. Under these conditions:

ρ = 28 lb per cu ft
x = 3.0 ft
k_1 = 1.91 per min
$G = (4)(8.33) = 33.32$ lb/(sq ft)(min)
$v_0 = \left(\frac{25{,}000}{100}\right)\left(\frac{2}{7000}\right)\left(\frac{1}{28}\right) = 0.00255$ lb equivalent Na per lb exchanger
u_0 = 6.0 lb equivalents Ca ion per million lb water
$\tau = (16)(60) = 960$ min

From Equation (41),

$$r = \frac{10^6\rho k_1 v_0^2 x}{G} = \frac{10^6(28)(1.91)(0.00255)^2(3)}{33.32} = 31.3$$

$$s = k_1u_0v_0\tau = (1.91)(6.0)(0.00255)(960) \qquad = 28.1$$

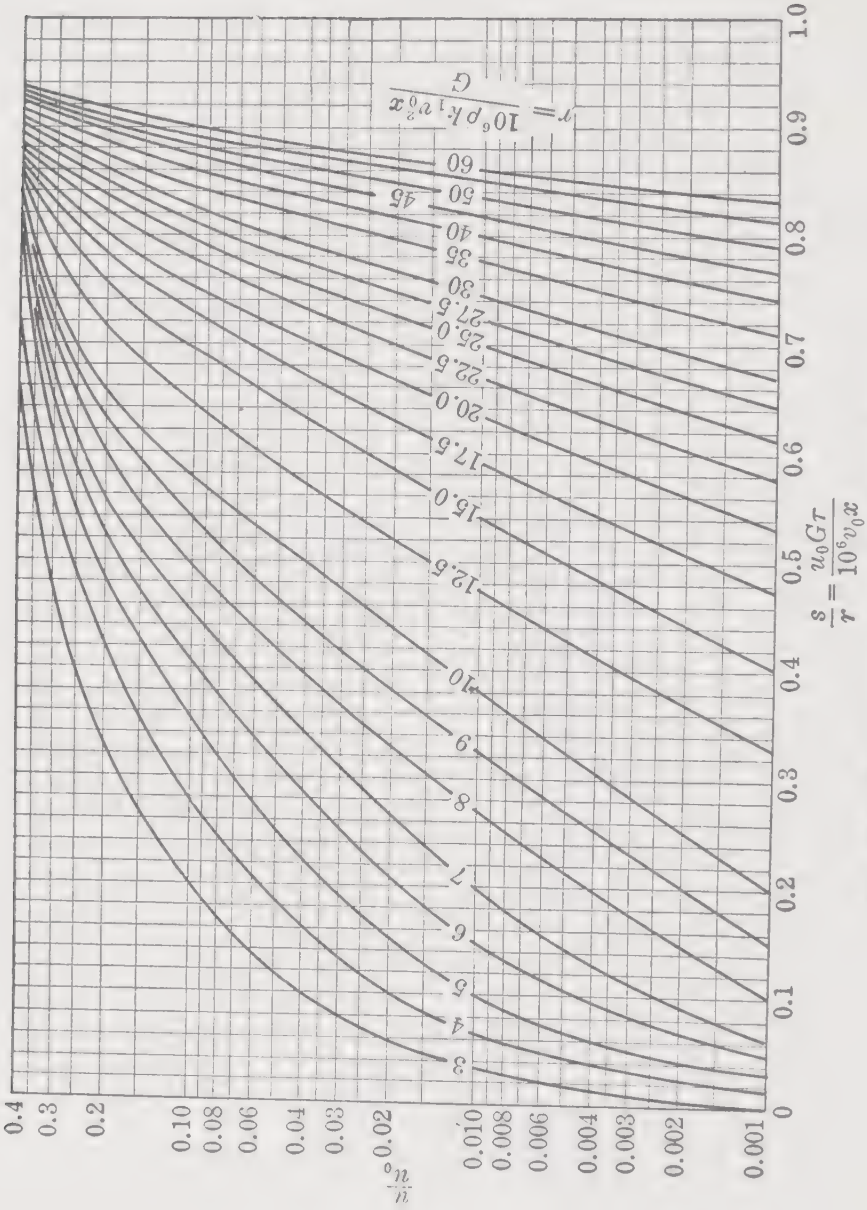

FIG. 214. Performance Chart for Water Softening.

(Reproduced in "C.P.P. Charts.")

From Equation (40),

$$\ln z + z = \ln s + s - r = \ln 28.1 + 28.1 - 31.3 = 0.14$$

or

$$z = 0.62$$

$$\frac{u}{u_0} = \frac{1 + \frac{1}{s}}{1 + \frac{1}{z}} = \frac{1.0356}{2.61} = 0.397$$

Hence $u = (0.397)(6.00) = 2.38$ lb equivalent of Ca^{++} per million lb of water leaving softener at the end of 16 hr

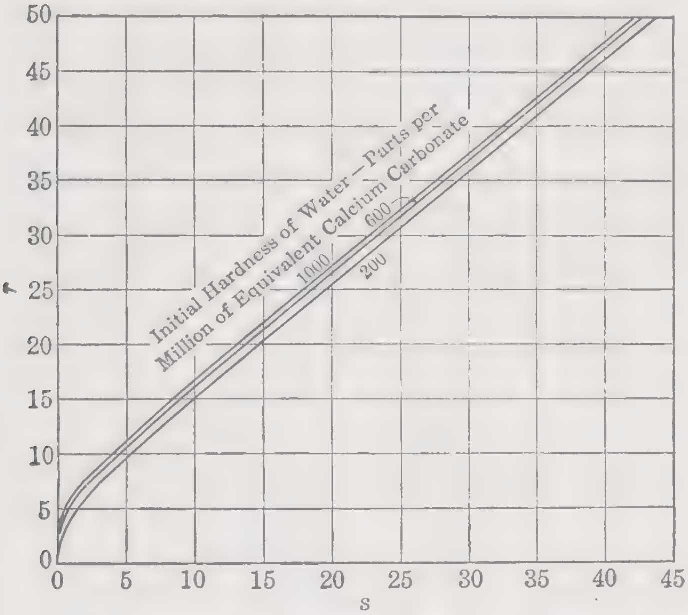

FIG. 215. Performance Chart for Softening Water to a Residual Hardness of 7 Parts per Million.

(Reproduced in "C.P.P. Charts")

In this manner, values of residual hardness can be calculated for any time, thickness of bed, rate of water flow, cation-exchange capacity of exchanger, and reaction velocity constant.

Use of Performance Charts. The preceding problem can be solved directly from the performance chart. Since $r = 31.3$ and $s = 28.1$, $s/r = 0.898$. The value of u/u_0 corresponding to these values of r and s/r is read from Fig. 214 as 0.36.

Illustration 4. In water softening the exchanger should be regenerated when the effluent water reaches a hardness of seven parts per million of calcium carbonate. Estimate the amount of water which can be treated in the system of Illustration 3 under this requirement.

From Fig. 215, when $r = 31.3$, and $u_0 = 6.0$, $s = 24.6$ or $\tau = 24.6/0.0292 = 844$ min (14.1 hr)

The water softened by 3 cu ft of mineral during this period is 844(4) = 3376 gal; the calcium carbonate is

$$\frac{(3376)(8.34)(300 - 7)}{10^6} = 8.24 \text{ lb } CaCO_3$$

or 19,200 grains of $CaCO_3$ are removed per cu ft of exchanger. The water softened by 1 cu ft of mineral under the aforementioned conditions is (4)(844)/3 = 1130 gal.

The reaction velocity constant of a cation exchanger can be obtained from the commercial performance of a thick bed by use of Fig. 214. It is necessary to start with a fully regenerated exchanger and to know its density, maximum cation-exchange capacity, and thickness. The initial hardness u_0 of the water, rate of water flow G, and exit hardness u, at end of a given time τ, must be measured.

Illustration 5. It is desired to estimate the reaction velocity constant k of a cation exchanger. A bed 3 ft in thickness is used, having a density of 28 lb per cu ft and a maximum cation-exchange capacity of 25,000 grains calcium carbonate per cu ft. Water having an initial hardness of 300 parts of calcium carbonate per million is passed through the exchanger at a rate of 4 gal per sq ft per min for 14.1 hr when the water leaving has a hardness of seven parts per million of $CaCO_3$.

$$u_0 = 6.0$$
$$v_0 = 0.00255$$
$$G = 33.32$$
$$\frac{u}{u_0} = 0.0233$$
$$y = 846 \text{ min}$$
$$\frac{s}{r} = \frac{(6)(33.32)(846)}{10^6(28)(0.00255)(3)} = 0.79$$

From Fig. 214, the intersection of $s/r = 0.79$ with $u/u_0 = 0.0233$ gives an r value of 32.

Thus
$$k_1 = \frac{rG}{10^6 \rho v_0^2 x} = \frac{(32)(33.32)}{10^6(28)(0.00255)^2(3)} = 1.95$$

The mathematical treatment and performance chart of cation exchangers can be extended to similar heterogeneous reactions in a batch process where one atom or ion in the fluid phase reacts with two atoms or active spots in the solid.

GAS ADSORPTION

The problem of estimating the changes in concentration in a fluid stream and in a bed of adsorbent where a process of adsorption proceeds intermittently presents formidable mathematical difficulties which have not been completely solved for the general case. For the special case where adsorption takes place from a dilute solution and where the equilibrium adsorption is directly proportional to the concentration, Marshall and Hougen[7] developed the following procedure.

The material balance over an elementary section of thickness dZ measured in the direction of fluid flow and of unit cross-sectional area for an elementary period of time $d\tau$ may be written as follows:

$$Gy\,d\tau = G\left[y + \left(\frac{\partial y}{\partial Z}\right) dZ\right] d\tau + \rho_B\, dZ \left(\frac{\partial w}{\partial \tau}\right) d\tau + \rho_G F_e \left(\frac{\partial y}{\partial \tau}\right) d\tau\, dZ \qquad (44)$$

where

G = mass velocity of adsorbate-free fluid, lb/(sq ft)(hr)
ρ_B = bulk density of solid, lb per cu ft
ρ_G = density of gas, lb per cu ft
F_e = external void fraction of bed
τ = time, hr
w = adsorbate content of solid, lb per lb of solid (adsorbate-free
y = adsorbate content of fluid stream, lb per lb of fluid (adsorbate-free basis)
Z = distance in bed measured in direction of flow, ft
The adsorbate is designated as component A.

The first term in Equation (44) represents the mass of component A entering the section in time $d\tau$, the second term the mass leaving the section, the third the change in the mass of component A present in the solid portion of the elementary volume, and the fourth term the change in the content of component A in the fluid portion of the elementary volume all in the element of time $d\tau$.

Equation (44) reduces to

$$-G\left(\frac{\partial y}{\partial Z}\right) = \rho_B\left(\frac{\partial w}{\partial \tau}\right) + \rho_G F_e\left(\frac{\partial y}{\partial \tau}\right) \qquad (45)$$

In a *nonflow process* where no fluid is being added or removed, the first term of Equation (45) is zero, and the material balance becomes

$$\rho_B\left(\frac{\partial w}{\partial \tau}\right) = -\rho_G F_e\left(\frac{\partial y}{\partial \tau}\right) \qquad (46)$$

In a *steady-flow process* the last term of Equation (45) becomes negligible if the fluid content of the bed is negligible compared with the volume of fluid passed through. In this case,

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[7] O. A. Hougen and W. R. Marshall, Jr., *Chem. Eng. Progress* **43**, 197 (1947). This mathematical development was originally prepared by these authors in a report by O. A. Hougen and F. W. Dodge entitled, "Drying of Gases," prepared for NDRC of OSRD, June 30, 1941 and now declassified for distribution through the Office of Technical Services, PB 23201, U.S. Department of Commerce (1946).

$$-G\left(\frac{\partial y}{\partial Z}\right) = \rho_B\left(\frac{\partial w}{\partial \tau}\right) \tag{47}$$

In gas adsorption where mass transfer through a gas film is the controlling factor, the rate of adsorption of component A can be expressed as follows:

$$r_A = K_G a_v (p_A - p_A^*) \tag{48}$$

where

r_A = lb-moles A adsorbed/(cu ft) (hr)
p_A = partial pressure of A in main gas stream, atmospheres
p_A^* = partial pressure of A in equilibrium with the adsorbate content of the solid, atmospheres
a_v = external area of solid particles, sq ft per cu ft
K_G = mass-transfer coefficient as defined by Equation (48)

For ideal-gas behavior, by Dalton's law,

$$\frac{p}{\pi - p} = \frac{yM_G}{M_A} \tag{49}$$

where π = total pressure
M_G = molecular weight of gas (adsorbate-free basis)
M_A = molecular weight of adsorbate gas A

At low concentrations of A, Equation (49) becomes

$$p = \frac{yM_G\pi}{M_A} \tag{50}$$

Equation (48) may then be written for these conditions as

$$r_A = K_G a_v \frac{M_G}{M_A} \pi(y - y^*) \tag{51}$$

Equation (51) may also be written in terms of the height of transfer unit H_{dG}, Equation (XX-37), page 984. Thus, for dilute gases where $p_f = \pi$,

$$r_A = \frac{G}{M_A H_{dG}}(y - y^*) \tag{52}$$

The changes in adsorbate content of the adsorbent and of the gas may be expressed in terms of the rate of adsorption given by Equation (52). Thus, for the solid adsorbent, expressing rate in pounds rather than in pound moles,

$$\rho_B\left(\frac{\partial w}{\partial \tau}\right) = \frac{G}{H_{dG}}(y - y^*) \tag{53}$$

Similarly, for the gas,

$$-G\left(\frac{\partial y}{\partial Z}\right) - \rho_G F_e\left(\frac{\partial y}{\partial \tau}\right) = \frac{G}{H_{dG}}(y - y^*) \qquad (54)$$

Equations (53) and (54) may be written as follows:

$$\left(\frac{\partial w}{\partial \tau}\right) = \beta(y - y^*) \qquad (55)$$

and

$$\left(\frac{\partial y}{\partial Z}\right) + \gamma\left(\frac{\partial y}{\partial \tau}\right) = -a(y - y^*) \qquad (56)$$

where

$$\left.\begin{aligned} \beta &= \frac{G}{\rho_B H_{dG}} \\ \gamma &= \frac{\rho_G F_e}{G} \\ a &= \frac{1}{H_{dG}} \end{aligned}\right\} \qquad (57)$$

The development of Equations (55) and (56) is restricted to ideal-gas behavior and low concentrations for which Equation (50) is satisfactory. In the general case the temperature in the bed may vary and y^* bears a complex relationship to w. Under these conditions an analytical solution is not available, and it is necessary to resort to the tedious graphical method discussed on page 1094.

Isothermal Adsorption with Linear Equilibrium. For the restricted case of isothermal adsorption analytical integration of Equations (55) and (56) is possible if it may be assumed that y^*, the equilibrium adsorbate content of the gas, is proportional to w the adsorbate content of the solid. This situation is approximated in many systems. Thus,

$$y^* = cw + \alpha \qquad (58)$$

where α = value of y^* where the linear portion of the equilibrium adsorbate content curve is extrapolated to a zero value of w.

Where α is not zero the following mathematical development holds strictly only for operation over the linear part of the equilibrium curve and does not extend to zero adsorbate content of solid.

For the majority of adsorption systems of industrial importance the absorbate content of the gas present in the bed at any instant is negligible in comparison to the total quantity of adsorbate passed through in an operating cycle. Under these conditions the term $\gamma(\partial y/\partial \tau)$ is negligible, and Equations (55) and (56) may be combined with (58) and written as follows:

$$\left(\frac{\partial w}{\partial \tau}\right) = b\left(\frac{y}{c} - w\right) \tag{59}$$

where

$$b = \beta c$$

$$-\left(\frac{\partial y}{\partial Z}\right) = a(y - cw) \tag{60}$$

The solution for this pair of partial-differential equations was developed by Hougen and Marshall[7] for the special condition where y is constant at $Z = 0$ for all values of τ, and w is zero at $\tau = 0$ for all values of Z.

This solution is in terms of the four dimensionless groups, $(y - y_0^*)/(y_0 - y_0^*)$, $(w - w_0^*)/(w_0 - w_0^*)$, aZ and $b\tau$.

Thus,

$$\frac{y - y_0^*}{y_0 - y_0^*} = 1 - e^{-b\tau}\int_0^{aZ} e^{-aZ}\, J_0(2i\sqrt{b\tau aZ})\,d(aZ) \tag{61}$$

$$\frac{w - w_0^*}{w_0 - w_0^*} = e^{-aZ}\int_0^{b\tau} e^{-b\tau}\, J_0(2i\sqrt{aZb\tau})\,d(b\tau) \tag{62}$$

where y_0 = mass of adsorbate per unit mass of adsorbate-free gas in the entering stream

w_0 = mass of adsorbate per unit mass of adsorbent in equilibrium with the entering gas

w_0^* = adsorbate content of bed, lb per lb solid (adsorbate-free basis) at $\tau = 0$. When the solid is free of adsorbate at zero time, $w_0^* = 0$

y_0^* = equilibrium adsorbate content of the fluid stream, lb per lb gas (adsorbate-free basis) at $\tau = 0$. When the solid is adsorbate free at zero time, $y_0^* = 0$

$i = \sqrt{-1}$

and J_0 = Bessel function of the first kind.[8]

Equations (61) and (62) are similar in form to those developed by Anzelius[9] for the analogous problem in heat transfer. For this latter problem Schumann[10] presented the solution in charts which were extended by Furnas[11] to high values of $2i\sqrt{b\tau aZ}$. Special forms of these charts applicable to the special case of gas adsorption as well as to heat transmission are shown in Figs. 216, 216a, and 217.

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[8] I. S. and E. S. Sokolnikoff, "Higher Mathematics for Engineers," McGraw-Hill Book Company.

[9] A. Anzelius, *Z. Angew. Math. Mech.*, **6**, 291 (1926).

[10] T. E. S. Schumann, *J. Franklin Inst.*, **208**, 405 (1929).

[11] C. C. Furnas, *Trans. Am. Inst. Chem. Engrs.*, **24**, 142 (1930).

Figures 216 and 216a show the composition of the gas stream as it progresses through the bed at different time intervals, and Fig. 217 shows the corresponding fractional saturation of the bed under the same circumstances. In Figs. 216 and 216a values of y/y_0 and in Fig. 217 values of w/w_0 are plotted against $b\tau$ for various values of aZ.

Heights of Transfer Units in Gas Adsorption. If mass transfer in the gas film were the only resistance to adsorption the value of H_d, the height of mass-transfer unit, could be calculated from Equations (XX-39–47), page 985. Actually, the over-all values of H_d and H_h are larger than given by these equations, because the entire superficial surface may not be available and the solid itself offers resistance to transfer.

From the experimental data of Ahlberg,[12] on the adsorption of water vapor from air by silica gel, Hougen and Marshall[7] found the over-all heights of mass- and heat-transfer units, H_{d0} and H_{h0} could be expressed by the following relationships.

$$H_{d0} = \frac{1.42}{a_v}\left(\frac{D_pG}{\mu}\right)^{+0.51} \tag{63}$$

$$H_{h0} = \frac{1.49}{a_v}\left(\frac{D_pG}{\mu}\right)^{+0.51} \tag{64}$$

These values are 3.57 times greater than the values calculated from the gas film alone. In establishing Equations (63) and (64) account was taken of the adiabatic operation of the bed with calculations of solid and air temperatures from the heats of adsorption and the energy balance of the system.

For silica gel the values of D_p and a_v given in Table LXII have been estimated for various Tyler standard mesh sizes.

TABLE LXII

PROPERTIES OF SILICA GEL

Mesh Size	D_p, ft	a_v, sq ft per cu ft
2–4	0.0220	117
4–6	0.0128	202
6–8	0.00909	284
8–10	0.00634	407
10–12	0.00576	448
12–14	0.00446	576
14–20	0.00320	805
20–28	0.00226	1140

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[12] J. E. Ahlberg, *Ind. Eng. Chem.*, **31**, 988–92 (1939).

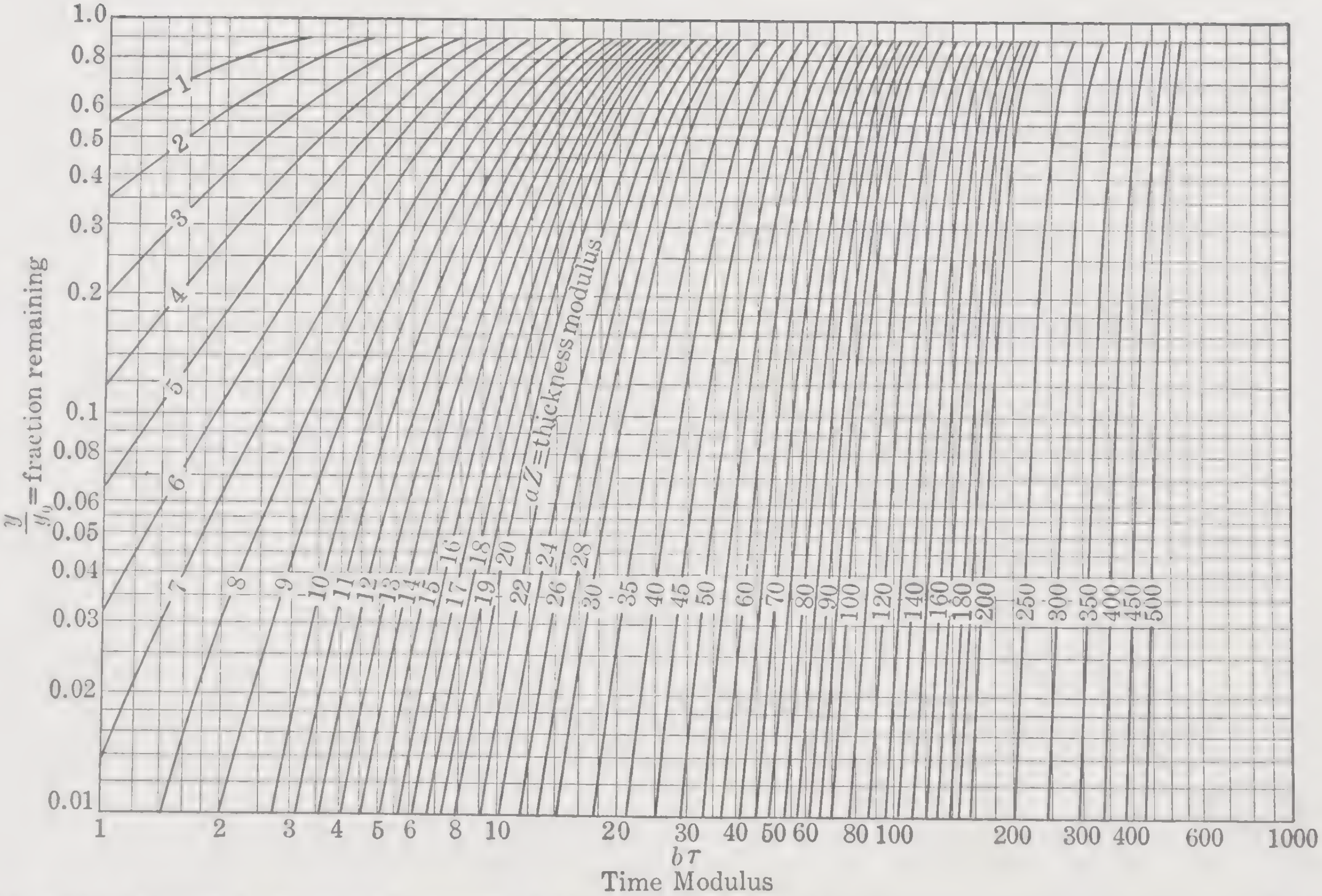

FIG. 216. Fraction of Adsorbate Remaining in a Fluid Stream after Adsorption by a Stationary Granular Bed.

(Reproduced in "C.P.P. Charts")

The equilibrium moisture content of a typical silica gel is given by the following relationship:

$$w = 0.55\left(\frac{p^*}{p_s}\right) \quad \text{or} \quad p^* = 1.82wp_s \tag{65}$$

where

p^* = partial pressure of water vapor in gas in equilibrium with the water adsorbed by the gel, atmospheres

p_s = vapor pressure of water at the existing temperature, atmospheres

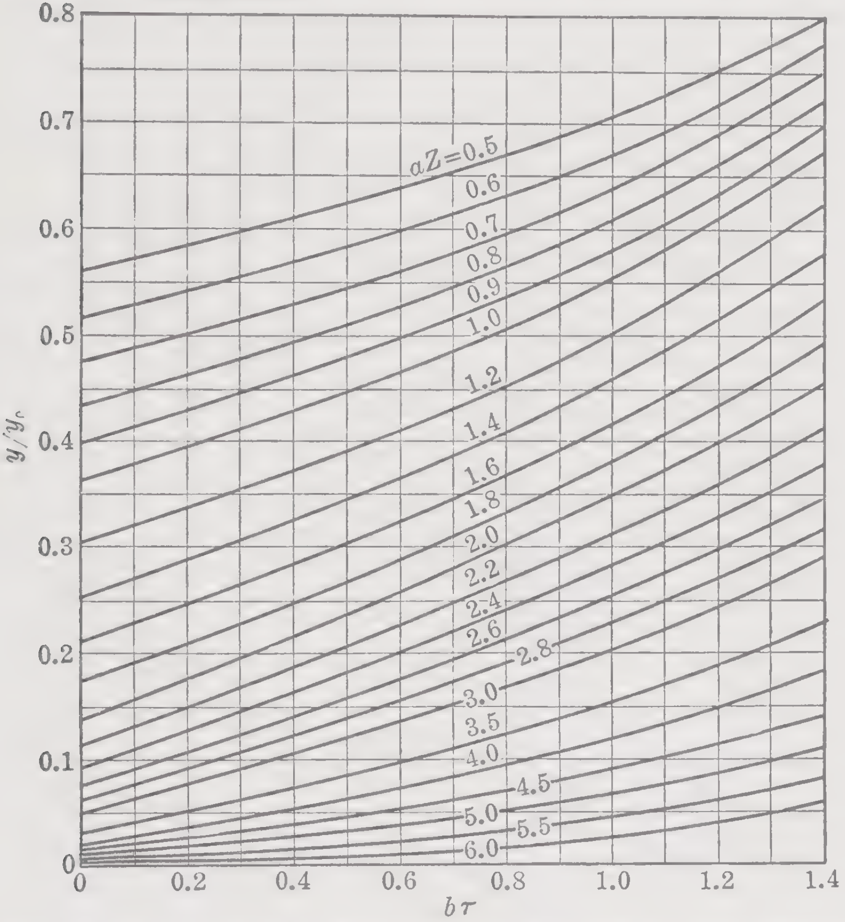

FIG. 216a. Fraction of Adsorbate Remaining in a Fluid Stream after Adsorption by a Stationary Granular Bed.
(Low Time Range)

The ratio p^*/p_s is the relative humidity of the gas in equilibrium with the gel. For the drying of air at atmospheric pressure, from Equation (50),

$$p^* = y^*\frac{M_G\pi}{M_A} = 1.62y^* \tag{66}$$

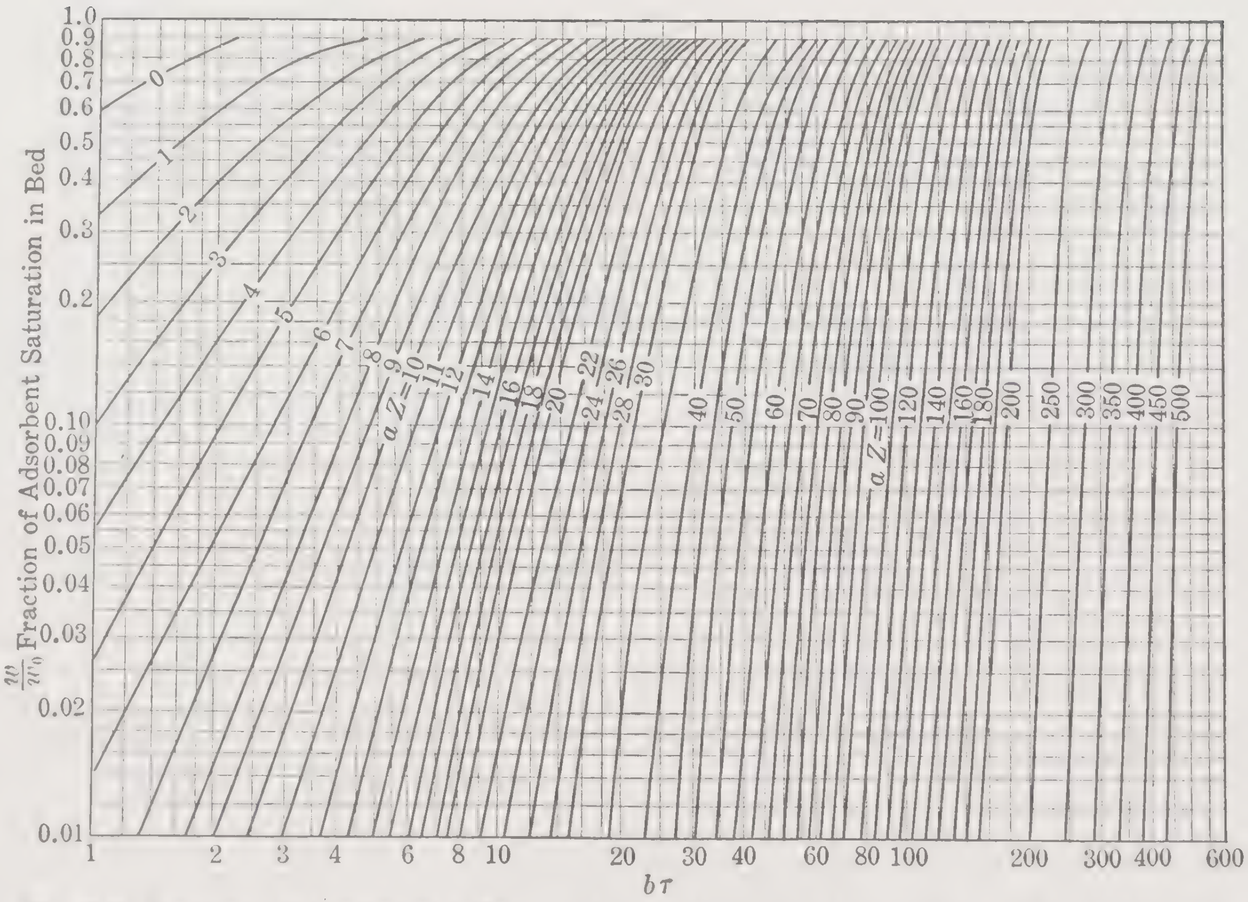

FIG. 217. Fractional Saturation of a Granular Bed in Adsorbing a Component from a Fluid Stream.
(Reproduced in "C.P.P. Charts")

Combining Equations (65) and (66) gives

$$y^* = \frac{1.82}{1.62} p_s w = cw \tag{67}$$

where

$$c = 1.122 p_s$$

For the special case of isothermal adsorption of water vapor on silica gel, from Equations (57) and (63),

$$a = \frac{1}{H_{d0}} = 0.703 a_v \left(\frac{D_p G}{\mu}\right)^{-0.51} \tag{68}$$

From Equations (57), (63), and (67),

$$b = \frac{Gc}{\rho_B H_d} = \frac{1.122 G p_s}{\rho_B H_d} = \frac{0.789\, G p_s a_v}{\rho_B} \left(\frac{D_p G}{\mu}\right)^{-0.51} \tag{69}$$

Illustration 6. Air is blown through a bed of initially dry silica gel, 1 ft in thickness. The air enters at 80°F and 80 per cent relative humidity ($y_0 = 0.0179$) at a linear velocity of 100 ft per min based on the total cross section. The gel is 6–8 mesh in size with a bulk density, ρ_B of 39 lb per cu ft. It is assumed that isothermal conditions are maintained by means of cooling coils in the bed. The following data are desired:

(*a*) The humidity of the air leaving the bed at the end of 2 hr.
(*b*) The average humidity of the air leaving the bed over a period of 2 hr.
(*c*) The moisture distribution in the bed at the end of 2 hr.
(*d*) The average moisture content of the bed at the end of 2 hr.

Data for calculations:

Density of gel, ρ_B = 39 lb per cu ft
Density of air entering, ρ_G = 0.0715 lb per cu ft

$$G = (100)(0.0715) = 7.15 \text{ lb}/(\text{sq ft})(\text{min})$$
$$\mu = 74.5(10^{-5}) \text{ lb}/(\text{ft})(\text{min})$$

From Table LXII,

$$D_p = 0.00909 \text{ ft}$$

$$a_v = 284 \text{ sq ft per cu ft}$$

$$\left(\frac{D_p G}{\mu}\right) = \frac{(0.00909)(7.15)10^5}{74.5} = 87.4$$

$$\left(\frac{D_p G}{\mu}\right)^{-0.51} = 0.1025$$

$$p_s\ (80°\text{F}) = 0.0345 \text{ atm}$$

From Equation (68),

$$a = 0.703(284)(0.1025) = 20.5/\text{ft}$$

From Equation (69),

$$b = 0.789 \frac{(7.15)(0.0345)}{39} (284)(0.1025) = 0.145/\text{min}$$

(*a*) Humidity of air leaving at end of 2 hr:

$$b_T = (0.145)(120) = 17.4$$
$$aZ = (20.5)(1) = 20.5$$

From Fig. 216

$$\frac{y}{y_0} = 0.34$$
$$y = (0.34)(0.0179) = 0.0061$$

(*b*) To determine the average humidity of the air leaving the bed it is necessary to integrate the outlet humidity over the 2-hr period. Values of y at different times are calculated as in part (*a*) and tabulated as follows:

min	b_T	y/y_0	y
0	0	0	0
20	2.9	0	0
40	5.8	0.003	0.00005
60	8.74	0.016	0.00029
80	11.6	0.065	0.00116
100	14.5	0.185	0.00331
120	17.4	0.340	0.0061

Graphical integration by plotting y against τ gives the average value of y as 0.0010 (Fig. 218).

(*c*) The moisture distribution in the bed at the end of 2 hr is determined from Fig. 217.

$$\tau = 120 \text{ min}, \qquad b_T = 17.4, \qquad y_0 = 0.0179$$

From Equation (65), $w_0 = 0.55(0.80) = 0.44$

Values of w/w_0 corresponding to selected values of aZ are read from Fig. 217 along a constant abscissa of $b_T = 17.4$ and tabulated as follows:

Z	aZ	w/w_0	w
0	0	1.00	0.44
0.2	4.1	1.00	0.44
0.4	8.2	0.92	0.405
0.6	12.3	0.78	0.344
0.8	16.4	0.57	0.25
1.0	20.5	0.30	0.132

The moisture distribution in the bed is shown graphically in Fig. 218a by plotting w against Z.

(*d*) The average moisture content of bed at end of 2 hr is obtained by a graphical integration of the relationship between w and Z from part (*c*) and found to be 0.348.

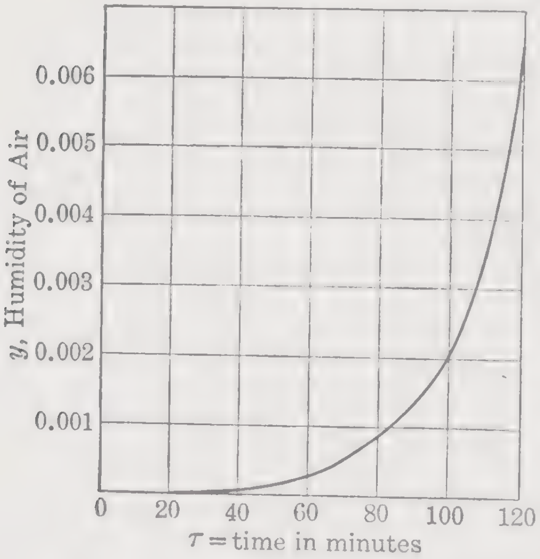

FIG. 218. Humidity of Air Leaving a Bed of Silica Gel, 1 Foot Thick.

For the adsorption of gases in highly dilute mixtures, nearly isothermal conditions prevail, and the assumptions made in Illustration 6 are satisfactorily accurate for many purposes.

Illustration 7. Benzene vapor is to be adsorbed from air in a solvent recovery plant by the air being passed downward through a bed of silica gel at 70°F and atmospheric pressure at a mass velocity (solvent-free) of 7.5 lb/(sq ft)(min). It is desired to operate for an adsorption period of 60 min with a minimum benzene recovery from the air of 90 per cent. The entering air contains 0.90 per cent benzene by volume. The silica gel is 4–6 mesh in size, having an external void fraction of 50 per cent and a bulk density of 39 lb per cu ft. For adsorption up to 20 per cent by weight (adsorbate-free basis) the weight of benzene adsorbed is directly proportional to the partial pressure of the benzene in the air in accordance with the equation $w = 1.67p^*/p_s$. The vapor pressure of benzene p_s at 70°F is 0.125 atm.

(*a*) Calculate the depth of bed required.

(*b*) Calculate the concentrations of benzene in the silica gel at the top, middle, and bottom of the bed at the end of 60 min.

(*a*) Depth of bed required:

From Table LXII, $D_p = 0.0128$ ft.;

$$a_v = 202$$

$$\mu = 74.5(10^{-5})\ \text{lb}/(\text{ft})(\text{min})$$

$$G = 7.5\ \text{lb}/(\text{sq ft})\ (\text{min})$$

$$\frac{D_pG}{\mu} = \frac{(0.0128)(7.5)(10^5)}{74.5} = 129.$$

$$\left(\frac{D_pG}{\mu}\right)^{-0.51} = 0.0825$$

From Equation (63),

$$a = \frac{1}{H_d} = 0.703a_v\left(\frac{D_pG}{\mu}\right)^{-0.51}$$

$$= (0.703)(202)(0.0825) = 11.8$$

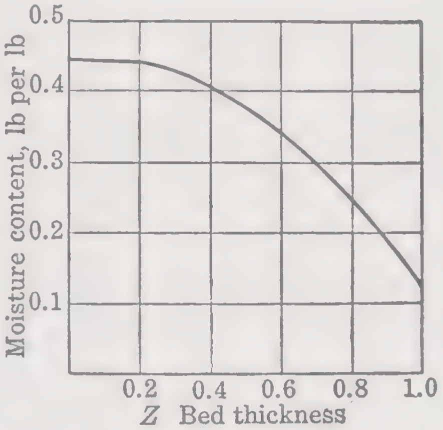

FIG. 218a. Moisture Distribution in a Bed of Silica Gel at the End of 2 Hr.

In order to evaluate b it is necessary to calculate c of Equations (58) and (59). Since from Equation (50) and since $w = 1.67p^*/p_s$, and $p^* = y^*\pi(29/78)$, $= wp_s/1.67$

$$c = \frac{y^*}{w} = \frac{p_s(78)}{\pi(29)(1.67)} = 1.60p_s/\pi$$

Then, from Equations (57) and (59):

$$b = \frac{1.60Gp_s}{\rho_B H_{dG}\pi} = \frac{(1.60)(7.5)(0.125)}{(39)(1/11.8)(1)} = 0.455/\text{min}$$

$$b_T = (0.455)(60) = 27.2$$

$$\frac{y}{y_0} = 0.10\ (90\%\ \text{removal})$$

From Fig. 216, where $b_T = 27.2$ and $y/y_0 = 0.10$; $aZ = 38$

$$Z = \frac{aZ}{a} = \frac{38}{11.8} = 3.22\ \text{ft}$$

(*b*) Concentration of benzene in silica gel at top, middle, and bottom of bed:

$$w_0 = 1.67\frac{p_0^*}{p_e} = \frac{1.67(0.009)}{0.125} = 0.120$$

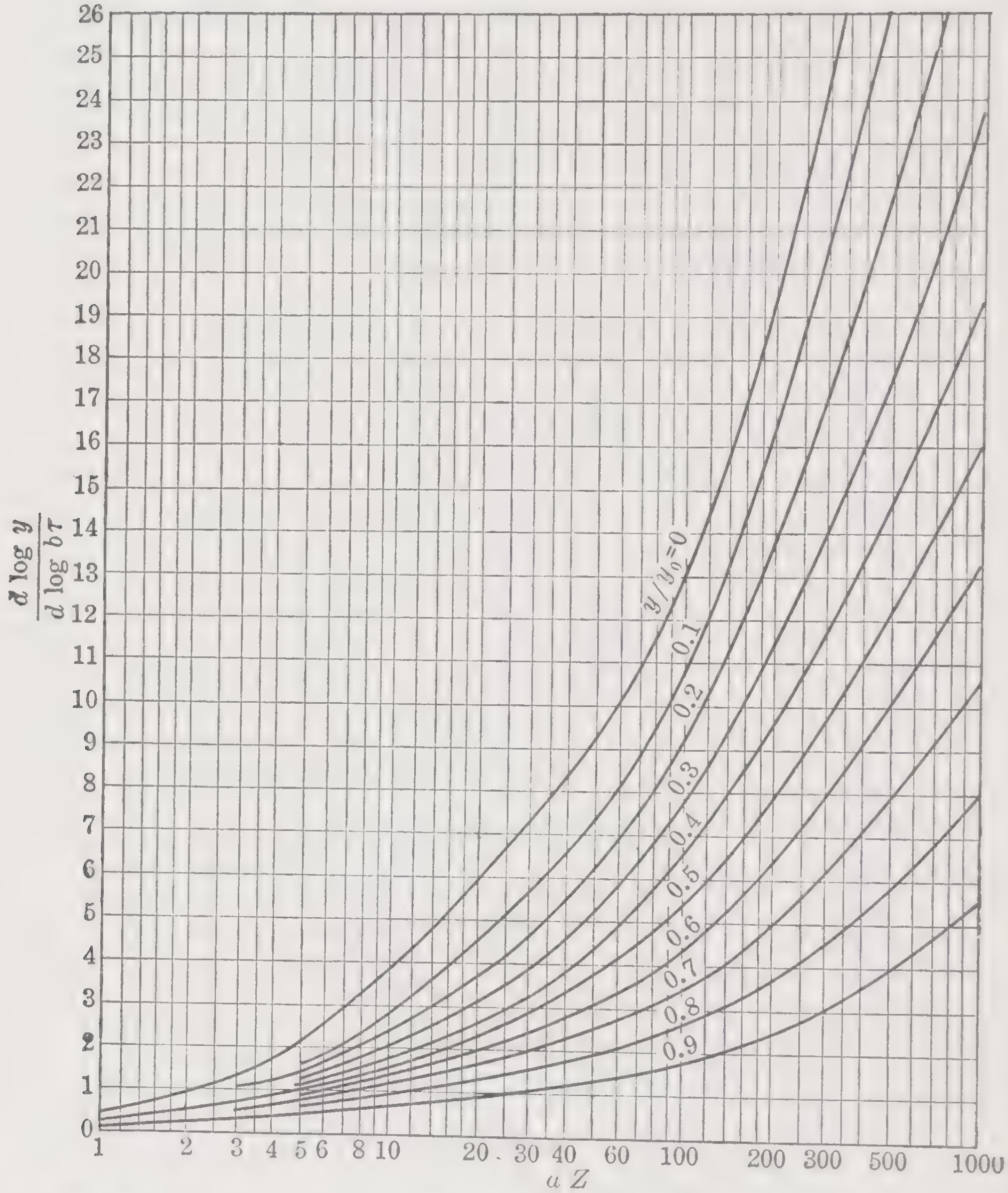

FIG. 219. Rate of Composition Change of a Fluid Stream Leaving a Bed of a Granular Adsorbent.

(Reproduced in " C.P.P. Charts ")

From part (*a*), $a = 11.8$; $b\tau = 27.2$

	Top	*Middle*	*Bottom*
Z	0	1.61	3.22
aZ	0	19.0	38.0
w/w_0 (from Fig. 217)	1.0	0.83	0.079
w	0.120	0.099	0.0095

Experimental Evaluation of Constants *a* and *b*. Where uncertainty prevails in the evaluation or calculation of the height of a transfer unit, values of a and b in Figs. 216 and 217 can be obtained directly from experimental data by measuring the adsorbate content of the effluent gas from a given bed over an extended period of time, provided the bed is initially free of adsorbate, nearly isothermal conditions are maintained, and the gas is supplied at a steady rate and fixed composition. By graphical differentiation of Fig. 216 the values of $(d \log y)/(d \log b\tau)$ were obtained and plotted in Figs. 219 and 220 as functions of aZ at different values of y/y_0.

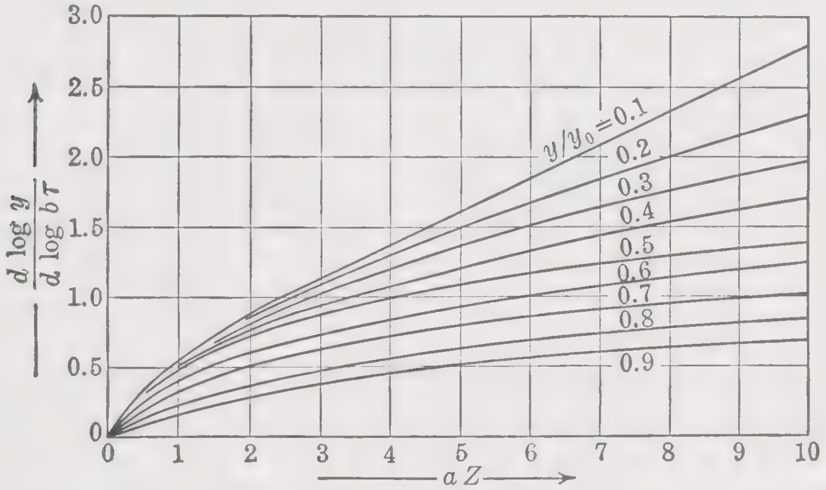

FIG. 220. Rate of Composition Change of a Fluid Stream Leaving a Bed of a Granular Adsorbent (At Low Values of aZ).

In establishing values of a and b from experimental data a plot of y against τ is made on logarithmic paper, and values of $(d \log y)/(d \log \tau)$ are obtained at values of y/y_0 in the experimental range by graphical differentiation. From Fig. 219 or 220 the corresponding value of aZ is determined and the value of a calculated from the known thickness of the bed. From the known values of y/y_0 and aZ, the values of $b\tau$ are obtained from Fig. 216, and from known values of time the values of b are calculated. From the known values of a_v, and D_pG/μ the constant in Equation (63) can be evaluated for the given experimental system. By employment of this equation values of a and b can be calculated for other conditions of operation from Equations (57) and (59).

Illustration 8. Air containing 0.58 mole per cent A is passed through bed of silica a gel kept at 25°C at a rate of 44.8 standard cu ft/(minute)(sq ft). The gel is 10–14 mesh and has a density of 44 lb/(cu ft). The bed is 2.0 ft deep. From measurements of the exit concentration of A at various intervals of time the values of time were obtained for given values of y/y_0, as shown in the first two columns of Table A. The values of $(d \log y)/(d \log \tau)$ were obtained from a plot of y/y_0 against τ on logarithmic paper. Values of aZ were obtained from Fig. 219 and a calculated from the thickness of the bed. From the values of y/y_0 and aZ, values of $b\tau$ were obtained from Fig. 216 and values of b calculated. These values are summarized in the following table:

TABLE A

ADSORPTION OF A BY SILICA GEL

$\frac{y}{y_0}$	Time, min	$\frac{d \log y}{d \log \tau}$	aZ	a, ft^{-1}	$b\tau$	b, min^{-1}
0.1	11.2	1.80	6.0	3.0	1.9	0.170
0.3	21.4	1.66	7.1	3.55	4.6	0.215
0.5	31.2	1.32	7.4	3.7	6.8	0.218
0.7	42.4	0.86	6.0	3.0	7.4	0.175
				Avg = 3.4		Avg = 0.195

Isothermal Adsorption with Complex Equilibrium. Where the relationship between the equilibrium adsorbate content of the adsorbent and that of the gas is not linear, or where the gas in the void of the bed is not negligible in comparison with the amount flowing through, the assumptions on which Equations (61) and (62) and Figs. 216–220 are based may lead to serious errors. In the former case it is necessary to resort to graphical integration of Equations (55) and (56).

By a change in variables the form of Equations (55) and (56) can be simplified to eliminate all constant terms and one partial derivative. The time variable τ is modified to allow for the time elapse from entrance to a position Z in the bed. As the front of a gas stream which enters the bed moves to a position Z units distant from the inlet, the time increases by the time required to reach that position. This time elapse can be calculated from the average linear velocity through the voids of the bed. Since the average fraction of free cross-sectional area is equal to the fraction of void volume, the average linear velocity is equal to $G/\rho_G F_e$, and the time elapsed in advancing from the entrance to position Z is $\rho_G F_e Z/G$ or γZ. The modified time variable then becomes $\tau - \gamma Z$. By this expedient one partial derivative and the constant γ are eliminated. The remaining constants a and β can then be eliminated by defining the new variables thus:

$$u = aZ \tag{70}$$

$$v = \beta(\tau - \gamma Z) \tag{71}$$

From Equation (70) it is evident that, when Z is zero, u is zero, and, from Equation (71), when $\tau = \gamma Z$, v is equal to zero.

Since w and y are functions of Z and τ, they are also functions of u and v and from Equation (XI-31):

$$dw = \left(\frac{\partial w}{\partial u}\right)_v du + \left(\frac{\partial w}{\partial v}\right)_u dv \tag{72}$$

$$dy = \left(\frac{\partial y}{\partial u}\right)_v du + \left(\frac{\partial y}{\partial v}\right)_u dv \tag{73}$$

Then

$$\left(\frac{\partial w}{\partial \tau}\right)_Z = \left(\frac{\partial w}{\partial u}\right)_v \left(\frac{\partial u}{\partial \tau}\right)_Z + \left(\frac{\partial w}{\partial v}\right)_u \left(\frac{\partial v}{\partial \tau}\right)_Z \tag{74}$$

$$\left(\frac{\partial y}{\partial Z}\right)_\tau = \left(\frac{\partial y}{\partial u}\right)_v \left(\frac{\partial u}{\partial Z}\right)_\tau + \left(\frac{\partial y}{\partial v}\right)_u \left(\frac{\partial v}{\partial Z}\right)_\tau \tag{75}$$

$$\left(\frac{\partial y}{\partial \tau}\right)_Z = \left(\frac{\partial y}{\partial u}\right)_v \left(\frac{\partial u}{\partial \tau}\right)_Z + \left(\frac{\partial y}{\partial v}\right)_u \left(\frac{\partial v}{\partial \tau}\right)_Z \tag{76}$$

From Equation (70):

$$\left(\frac{\partial u}{\partial Z}\right)_\tau = a \tag{77}$$

$$\left(\frac{\partial u}{\partial \tau}\right)_Z = 0 \tag{78}$$

From Equation (71):

$$\left(\frac{\partial v}{\partial Z}\right)_\tau = -\beta\gamma \tag{79}$$

$$\left(\frac{\partial v}{\partial \tau}\right)_Z = \beta \tag{80}$$

By substituting Equations (80), (78), and (55) into (74), there results

$$\left(\frac{\partial w}{\partial v}\right)_u = (y - y^*) \tag{81}$$

By substituting Equations (79), (80) into (75) and (76), and combining with Equation (56), there results

$$\left(\frac{\partial y}{\partial u}\right)_v = -(y - y^*) \tag{82}$$

A graphical method of double stepwise integration of Equations (81) and (82) has been developed after the pattern of Grossman.[13] Thus in terms of finite increments,

$$\left(\frac{\Delta y}{\Delta u}\right)_v = -(y_m - y_m^*) \tag{83}$$

where mean values are taken over the interval Δu and

$$\left(\frac{\Delta w}{\Delta v}\right)_u = (y_m' - y_m^{*\prime}) \tag{84}$$

where mean values are taken over the interval Δv. The relationship between y^* and w is obtained from isothermal equilibrium-adsorption measurements which may be expressed graphically for any system.

The graphical solution for isothermal adsorption follows in three steps. The adsorbate content of the gas stream as a function of time must be known at $Z = 0$ and hence at $u = 0$. The adsorbate content of the bed must be known when $\tau = 0$. Since the initial adsorbate content of the bed at any location is unchanged during the lapse of time γZ, the time required in passing to location Z, it follows from Equation (71) that the adsorbate content of the bed is the same at $v = 0$ as when $\tau = 0$.

The first step of the solution is to establish the adsorbate content of the gas at zero value of v as a function of u; the second step is to establish the adsorbate content of the bed at zero value of u, as a function of v. In the third step all other values of y and w are obtained for successive increments of Δu and Δv.

In designating values of w, y, and y^* at different intervals of distance and periods of time double subscripts are used, the first subscript designates increments of u and the second increments of v. Thus, the symbol y_{01} indicates the value of y at $0\,\Delta u$ and $1\,\Delta v$, the symbol w_{12} indicates the value of w at $1\,\Delta u$ and $2\,\Delta v$.

The general objective is shown in Fig. 221, where values of y, y^*, and w are plotted against increments of u for different intervals of v. The mean values over the interval Δu are represented as y_m, y_m^* and w_m, and the mean values over the interval Δv by the period values y'_m, $y^{*\prime}_m$ and w'_m. The circled points represent the initial given conditions.

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[13] L. V. Grossman, *Trans. Am. Inst. Chem. Engrs.*, **42**, 535, (1946).

Step I. In Fig. 222, the initial distribution of A in the bed is known and plotted against Δu. The corresponding values of y^* are obtained from adsorption-equilibrium data. The composition of the entering gas stream is known and designated as y_{00} and in this case is taken as constant with v at $u = 0$. From the value of w_m at $\frac{1}{2}\Delta u$, the corresponding value of y^*_m is obtained from adsorption-equilibrium data. From this point a horizontal line is projected of unit value in u to point B. For example, if $\Delta u = 0.2$ the length of the horizontal line is $5\Delta u$. A straight line is then drawn connecting y_{00} with B. The intersection of this line with the $1\Delta u$ line gives the desired value of y_{10}, and y_m is its intersection with the $\Delta u/2$ vertical line. The validity of this procedure is evident from the geometry of Fig. 222, where, from the relationship of similar triangles,

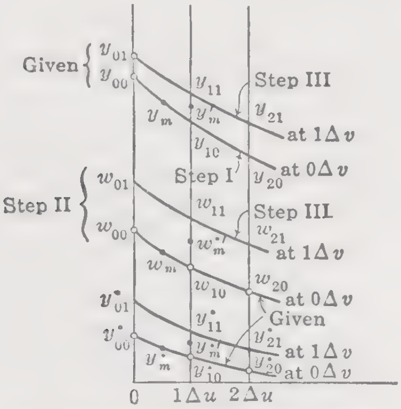

Given
y_{01}
y_{00}
y_{11}
Step III
y_m
y^*_m
y_{21}
at 1Δv
y_{10}
Step I
y_{20}
at 0Δv
Step II
w_{01}
w_{00}
w_{11}
Step III
w_{21}
w^*_m
at 1Δv
w_m
w_{10}
w_{20}
at 0Δv
y^*_{01}
Given
y^*_{11}
y^*_{00}
y^*_{21}
at 1Δv
y^*_m
y^*_m
y^*_{10}
y^*_{20}
at 0Δv
0
1Δu
2Δu

FIG. 221. Calculation of Concentration Gradients in Adsorption of Gases by a Granular Bed.

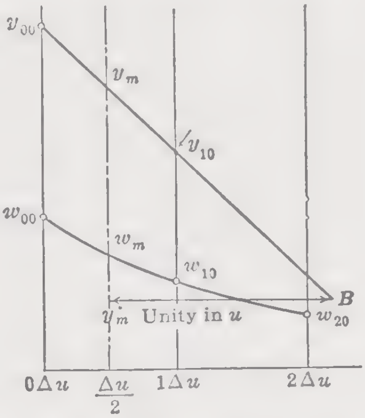

y_{00}
y_m
y_{10}
w_{00}
w_m
w_{10}
B
y^*_m Unity in u
w_{20}
0Δu
$\frac{\Delta u}{2}$
1Δu
2Δu

FIG. 222. Step I. Calculation of y at Zero Value of v.

$$\frac{y_{00} - y_{10}}{\Delta u} = -\frac{y_m - y^*_m}{1} = -\frac{\Delta y}{\Delta u} \tag{85}$$

in agreement with Equation (83).

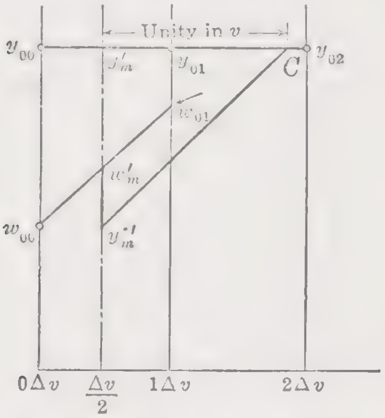
Successive values of y_{20}, $y_{30} \cdots$ are obtained in a similar manner with successive increments of Δu.

For the special case where the solid is initially adsorbate-free, $y^* = 0$ at $v = 0$, and Equation (82) is integrated to give

$$\ln \frac{y_0}{y} = u \quad (\text{at } v = 0) \tag{86}$$

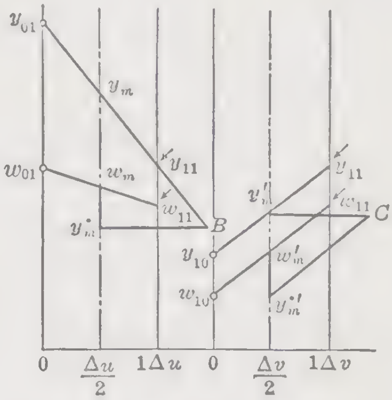
Step II. In step II it is desired to establish the adsorbate content of the solid at the entrance of the bed ($u = 0$) for various values of v. The adsorbate content of the entering gas is plotted against v in Fig. 223. In this case a constant value of y is assumed at $u = 0$ for all values of v.

The value of w_{00} is known and plotted. A mean value y'_m is obtained at $\Delta v/2$. A horizontal line of length equal to unity in v is extended horizontally from y'_m to C. Parallel lines are drawn through C and w_{00} such that at $\Delta v/2$, w'_m and $y^{*\prime}_m$ are in equilibrium. The intersection of the w line with the Δv vertical line gives the desired value of w_{01}. The validity of this procedure is evident from the geometry of Fig. 223, where, from the relations of similar triangles,



y_{00}
Unity in v
y'_m
y_{01}
y_{02}
C
w_{01}
w'_m
w_{00}
$y^{*\prime}_m$
$0\Delta v$
$\frac{\Delta v}{2}$
$1\Delta v$
$2\Delta v$

FIG. 223. Step II. Calculation of w at Zero Value of u.



y_{01}
y_m
y_{11}
w_{01}
w_m
w_{11}
y^*_m
B
y'_m
y_{11}
w_{11}
C
y_{10}
w'_m
w_{10}
$y^{*\prime}_m$
0
$\frac{\Delta u}{2}$
$1\Delta u$
0
$\frac{\Delta v}{2}$
$1\Delta v$

FIGS. 224–225. Step III. Evaluation of y and w Except at Zero Values of u and v.

$$\frac{w_{01} - w_{00}}{\Delta v} = \frac{y'_m - y^{*\prime}_m}{1} = \frac{\Delta w}{\Delta v} \tag{87}$$

in agreement with Equation (84). Succeeding values of w at zero values of u are obtained in the same manner for successive increments of Δv.

In the usual case where the gas enters the bed at constant composition and where equilibrium adsorption can be expressed by an equation, step II can be solved analytically. At $u = 0$, $y = y_0$, and where $y^* = mw^n$, Equation (81) becomes

$$v = \int_0^w \frac{dw}{y_0 - mw^n} \quad \text{(where } u = 0\text{)} \tag{88}$$

A graphical integration is required where n is not an integer.

Step III. With the establishment of the boundary conditions for both gas and solid the concentration of both gas and solid for succeeding increments not at zero values of either u or v is obtained by a combination of the methods illustrated, in Figs. 222, and 223, and shown in Figs. 224, and 225. For example, the next point to establish is w_{11} and y_{11}.

On Fig. 224, values of y_{01} and w_{01} and on Fig. 225 values of y_{10} and w_{10} are located from previous steps I and II, respectively. The values of y_{11} and w_{11} are established on each chart by the respective methods used in Figs. 221 and 222. Adjustments of the two figures must be made according to their geometry until points y_{11} and w_{11} agree on both charts. A mechanical device fulfilling the geometry of the two figures may be used to adjust the two figures readily. It is required in Fig. 224 that the linkage of lines pivots on y_{01} and w_{01}, that w_m and y_m^* are in equilibrium and are free to move along the vertical $\Delta u/2$, and that line y_m^*B is horizontal and of unit length in u. Points y_{11} and w_{11} are free to move along the vertical $1\Delta u$. It is required in Fig. 225 that the linkage of lines pivots on y_{10} and w_{10}, that w'_m and $y_m^{*\prime}$ are in equilibrium and are free to move along the vertical $\Delta v/2$, that line y'_mC is horizontal and of unit length in v and that lines $w_{10}w_{11}$, and $y_m^{*\prime}C$ are parallel.

It should be noted that this graphical method was developed for dimensionless time and distance parameters. However, the solution arrived at for a specific system and boundary conditions is a general solution for other variable conditions of operation.

Unsteady Heat Transmission in Granular Beds. As originally developed by Schumann[10] and Furnas[11] charts similar to Figs. 216 and 217 were used for calculating temperature changes in both gas stream and bed where heat was transferred between a flowing gas and a stationary granular bed in the absence of heat effects due to chemical reactions and where constant values of heat-transfer coefficients and thermal properties could be assumed. To use these charts for heat transmission the following replacements of symbols should be made.

$$\text{Substitute,}\qquad \left.\begin{aligned} &\frac{t - T_0}{t_0 - T_0} \quad \text{for} \quad \frac{y}{y_0} \\ &\frac{T - T_0}{t_0 - T_0} \quad \text{for} \quad \frac{w}{w_0} \\ &\frac{Ua_v}{C_pG} = \frac{1}{H_{h0}} \quad \text{for} \quad a \\ &\frac{Ua_v}{\rho_b C_S} \quad \text{for} \quad b \end{aligned}\right\} \qquad (89)$$

where t = temperature of gas
t_0 = temperature of gas entering
T = temperature of solid
T_0 = initial temperature of solid
U = over-all heat transmission coefficient, per unit area
H_{h0} = over-all height of heat-transfer unit
C_p = specific heat of gas
C_S = specific heat of solid

Where the thermal resistance of the solid is negligible, compared with the gas, and where the total superficial area of the granular solid is available for heat transfer, the over-all heat-transmission coefficient is equal to that of the gas film, $U = h_G$. The heat-transmission coefficient h_G of the gas film can be estimated from the Equations (XX-40, 45, 47), pages 985.

NONISOTHERMAL REACTIONS IN THE UNSTEADY STATE

Grossman[13] has developed a graphical method of establishing the unsteady-state time–temperature gradients in a granular bed through which a reacting fluid is flowing. This method is applicable to general heterogeneous reactions involving a fixed bed of solid reactant and to such problems as the temperature fluctuations in a checkerbrick or pebble-bed regenerator, to the period required for heating or cooling a reactor to a steady state, or to the burning of the carbonaceous deposit in the regeneration of a catalyst. Adiabatic conditions and a uniform velocity throughout any cross section of the bed are postulated. On this basis temperature–time position relationships may be developed to correspond to any specified initial temperature distribution of the solid and time–temperature relation for the entering fluid. The effects of variations in the thermal properties of the solid and fluid are readily taken into account.

In the development given herewith the chemical reaction is assumed to take place on the surface of the solid so that for an exothermic reaction the temperature of the solid is greater than that of the fluid. A differential energy balance is set up for the transfer of heat from the surface of the solid to the fluid in an element of the bed of unit cross-sectional area and of thickness dZ. For the fluid, the temperature changes are expressed by

$$C_G \rho_G F_e \left(\frac{\partial t_G}{\partial \tau}\right)_Z + (C_G G)\left(\frac{\partial t_G}{\partial Z}\right)_\tau = h a_v (t_S - t_G) \tag{90}$$

Similarly, for the solid,

$$C_S\rho_b\left(\frac{\partial t_S}{\partial \tau}\right)_Z = -ha_v(t_S - t_G) + r\,\Delta H\rho_b \tag{91}$$

where

C_G = specific heat of fluid
ρ_G = density of fluid
t_G = temperature of fluid
t_S = temperature of solid
C_S = specific heat of solid
Z = distance from the inlet of the bed
h = heat-transmission coefficient per unit area of solid
a_v = external area of solid per unit volume
G = mass velocity of fluid stream, mass/(area)(time)
r = rate of reaction, adsorption, or desorption, moles of A converted, adsorbed, or desorbed per unit time per unit mass of solid
ΔH = heat of reaction per mole of reactant A
ρ_b = bulk density of solid bed
F_e = external void fraction of solid bed

Let

$$\frac{ha_v}{C_S\rho_b} = k_1 \quad \text{and} \quad \frac{ha_v}{C_G\rho_B F_e} = \frac{G}{H_h\rho_G F_e} = k_2 \tag{92}$$

where H_h = height of a heat-transfer unit, Equation (XX-38), page 984. Then Equations (90) and (91) become

$$\left(\frac{\partial t_G}{\partial \tau}\right)_Z + \left(\frac{G}{F_e\rho_G}\right)\left(\frac{\partial t_G}{\partial Z}\right)_\tau = k_2(t_S - t_G) \tag{93}$$

$$\left(\frac{\partial t_S}{\partial \tau}\right)_Z = -k_1(t_S - t_G) + \frac{r\,\Delta H}{C_S} \tag{94}$$

Equations (93) and (94) may be simplified by transforming them in terms of two new variables u' and v' to replace Z and τ. By the procedure followed in the development of Equations (81) and (82) it is found that these variables are properly defined as follows:

$$u' = \frac{k_2F_e\rho_GZ}{G} = \frac{Z}{H_h} \tag{95}$$

$$v' = k_1\left(\tau - \frac{\rho_GF_e}{G}Z\right) \tag{96}$$

In terms of these variables Equations (93) and (94) reduce to

$$\left(\frac{\partial t_G}{\partial u'}\right)_{v'} = (t_S - t_G) \tag{97}$$

$$\left(\frac{\partial t_S}{\partial v'}\right)_{u'} = -(t_S - t_G) + \frac{r\,\Delta H}{C_S k_1} \tag{98}$$

For finite increments Equations (97) and (98) become

$$\left(\frac{\Delta t_G}{\Delta u'}\right)_{v'} = (t_{S_m} - t_{G_m}) \tag{99}$$

$$\left(\frac{\Delta t_S}{\Delta v'}\right)_{u'} = -\,(t'_{S_m} - t'_{G_m}) + B_m \tag{100}$$

where

$$B_m = \left(\frac{r\,\Delta H \rho_b H_h}{G C_G}\right)_m \tag{101}$$

Reaction Rates Independent of Conversion. Equations (99) and (100) can be solved by a stepwise graphical procedure similar to that discussed for Equations (83) and (84) in the restricted case where both the rate of reaction r and the heat of reaction ΔH can be assumed to be independent of conversion and functions only of temperature. Such an assumption with respect to r is justified only in the case of a fluid stream carrying a large excess of reactants or where as a result of the reaction mechanism the rate is substantially independent of composition. In such a case the solution is carried out in three steps similar to those of Figs. 221–225. The initial temperature distribution in the solid (at $v = 0$) is known. The temperature of the entering gas stream as a function of time is also known. The heat of reaction and the rate of reaction are known as functions of temperature. The first step is to establish the temperature of the gas at zero value of v' as a function of u', the second step is to establish the temperature of the bed as a function of v' at zero value of u'. In the third step other values of temperature are obtained for successive increments of $\Delta u'$ and $\Delta v'$.

In designating values of t_G and t_S at different intervals of distance and periods of time double subscripts are used; the first subscript designates increments of u' and the second increments of v'. Thus, the symbol t_{G01} indicates the temperature of the gas at $0\,\Delta u'$ and $1\,\Delta v'$, the symbol t_{S12} indicates the temperature of the solid at $1\,\Delta u'$ and $2\,\Delta v'$.

The general objective of the calculations is shown in Fig. 226 where t_S and t_G are plotted against increments of u' for different time intervals v'. The mean values over the interval $\Delta u'$ are represented as t_{G_m} and

t_{S_m} and the mean values over the interval $\Delta v'$ as t'_{G_m} and t'_{S_m}. The circled points represent the initial given conditions.

Step I. In Fig. 227 the initial known temperature of the bed is plotted against $\Delta u'$. The temperature of the entering gas stream is known and designated as t_{G00}. The first step is to establish the temperature of the gas stream as it first progresses through the bed (at $v' = 0$). The establishment of the first point t_{G10} is indicated in Fig. 227. From the mean temperature of the solid t_{S_m} at the interval $\Delta u'/2$ a horizontal line is projected of unit length in terms of u' to point B. (If $\Delta u' = 0.1$, then the length of the horizontal line is $10\ \Delta u'$). A straight line is drawn connecting B with t_{G00}. The intersection of this line with the $1\Delta u'$ line gives the desired temperature t_{G10}. The validity of this procedure is evident from the geometry of Fig. 227 where, from the relationship of similar triangles,

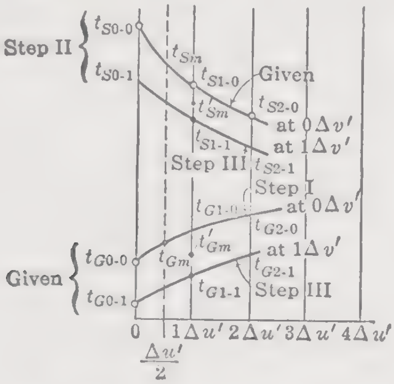

Step II
$t_{S0\text{-}0}$
$t_{S0\text{-}1}$
t_{Sm}
$t_{S1\text{-}0}$
Given
t'_{Sm}
$t_{S2\text{-}0}$
at 0 Δv′
$t_{S1\text{-}1}$
at 1 Δv′
Step III
$t_{S2\text{-}1}$
Step I
$t_{G1\text{-}0}$
at 0 Δv′
$t_{G2\text{-}0}$
t'_{Gm}
at 1 Δv′
Given
$t_{G0\text{-}0}$
t_{Gm}
$t_{G2\text{-}1}$
$t_{G0\text{-}1}$
$t_{G1\text{-}1}$
Step III
0
1Δu′
2Δu′
3Δu′
4Δu′
$\frac{\Delta u'}{2}$

FIG. 226. Calculation of Temperature Gradients in a Granular Bed.

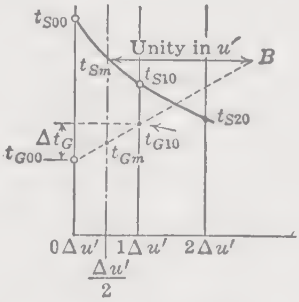

t_{S00}
Unity in u′
B
t_{Sm}
t_{S10}
t_{S20}
Δt_G
t_{G10}
t_{G00}
t_{Gm}
0Δu′
1Δu′
2Δu′
$\frac{\Delta u'}{2}$

FIG. 227. Step I. Calculation of Gas Temperatures at Zero Values of v'.

$$\frac{t_{G10} - t_{G00}}{\Delta u'} = \frac{\Delta t_G}{\Delta u'} = t_{S_m} - t_{G_m} \tag{102}$$

in agreement with Equation (99). Successive values of t_{G20}, t_{G30} are obtained in a similar manner with successive increments of $\Delta u'$.

For the common case where the solid is initially at a uniform temperature, Equation (97) can be integrated directly to give

$$\ln \frac{t_{S0} - t_G}{t_{S0} - t_{G0}} = u', \quad (\text{at } v' = 0) \tag{103}$$

Step II. In Step II it is desired to establish the temperature of the solid at the entrance of the bed ($u' = 0$) for various values of v'. The temperature of the entering gas is plotted against v'. The values of t_{S00} are known and plotted. A mean value of t'_{G_m} is obtained at $\Delta v'/2$.

The value of B_m is calculated at the average gas temperature t'_{G_m} and added to t'_{G_m} to give point C. A horizontal line CD is extended equal in length to a unit value of v'. A straight line $t_{S00}D$ is constructed. The intersection of this line with the $\Delta v'$ line gives the desired value of t_{S01}. The validity of this procedure is evident from the geometry of Fig. 228 where, from the relation of similar triangles,

$$\frac{\Delta t_S}{\Delta v'} = -\frac{(t'_{S_m} - t'_{G_m})}{1} + B_m = \frac{t_{S00} - t_{S01}}{\Delta v'} \qquad (104)$$

in agreement with Equation (100). Succeeding values of t_S at zero values of u' are obtained in the same manner for successive increments of $\Delta v'$.

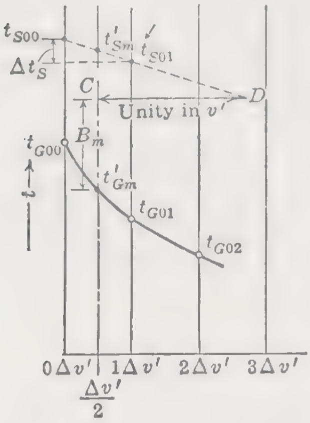
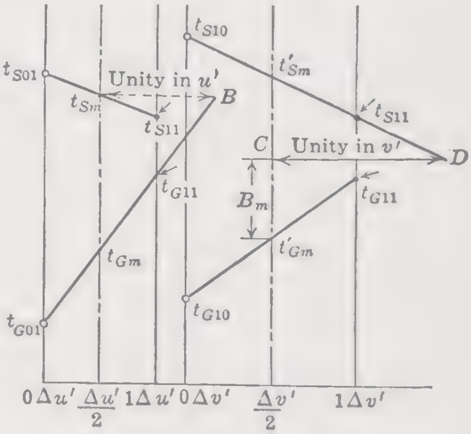

t_{S00}
t'_{Sm}
t_{S01}
Δt_S
C
D
Unity in v'
B_m
t_{G00}
t
t'_{Gm}
t_{G01}
t_{G02}
$0\Delta v'$
$\frac{\Delta v'}{2}$
$1\Delta v'$
$2\Delta v'$
$3\Delta v'$

FIG. 228. Calculation of Temperatures of the Solid at Zero Values of u.

Step III. With the establishment of the boundary conditions for both gas and solid, temperatures of both gas and solid for succeeding increments not at zero values for either u' or v' are obtained by a combination of the methods illustrated in Figs. 227 and 228 and shown in Figs. 229 and 230. For examples, the next points to be established are t_{S11} and t_{G11}.

On Fig. 229, values of t_{G01} and t_{S01} and on Fig. 230 values of t_{G10} and t_{S10} are located from previous steps I and II, respectively. The values of t_{G11} and t_{S11} are established on each chart by the respective methods of Figs. 227 and 228. Simultaneous adjustment of the two figures must be made according to their geometry until points t_{G11} agree on both charts, and similarly t_{S11}. A mechanical device fulfilling the geometry of the two figures may be used to obtain agreement readily. It is required in Fig. 229 that the linkage of lines pivots on points t_{S01} and t_{G01}, and that the line $t_{S_m}B$ is horizontal and of unit length in u'. Points t_{S11} and t_{G11} are free to move along the vertical line $\Delta u'$. It is required in Fig. 230 that the linkage of lines pivots on points t_{G10} and t_{S10}, and that the points C, t'_{S_m} are spaced at an interval B_m, depending upon the rate and heat of reaction,


t_{S10}
t_{S01}
Unity in u'
t'_{Sm}
t_{Sm}
B
t_{S11}
t_{S11}
C
Unity in v'
D
t_{G11}
B_m
t_{G11}
t'_{Gm}
t_{Gm}
t_{G10}
t_{G01}
$0\Delta u'$
$\frac{\Delta u'}{2}$
$1\Delta u'$
$0\Delta v'$
$\frac{\Delta v'}{2}$
$1\Delta v'$

FIGS. 229–230. Step III. Evaluation of t_G and t_S at Zero Values of u' and v'.

and are both free to move along the vertical $\Delta v/2$, that line CD is horizontal and of unit length in v'. Succeeding values of gas and solid temperature are obtained in a similar manner.

General Case. The procedure illustrated in Figs. 227–230 required knowledge of the reaction rate r at all points in the reactor. In the general case r is a function of conversion and composition as well as of temperature. Under such conditions it is necessary to evaluate simultaneously the distribution of conversion and composition along with temperature as the stepwise procedure is carried out. This involves combination of equations of the form of (83) and (84) for the evaluation of conversions with Equations (99) and (100) for temperature. The simultaneous solution of the four equations is carried out by a stepwise procedure similar to that used for either pair individually but complicated by the necessity of additional successive approximations which result from the fact that the temperature changes and conversion changes in any increment are interdependent.

A common example is in the adiabatic adsorption of a gas by a stationary bed. The rate of adsorption is a function of the adsorbate content of both the gas and the solid as well as of the temperature of each and can be determined experimentally and expressed graphically for even the most complex cases. Similarly, the differential heat of adsorption is a function of temperature and the adsorbate content of the adsorbent which may be expressed in either graphical or analytical form. From these two relationships working charts may be prepared which for a specific problem relates B_m of Equation (101) to temperature and the adsorbate content of both the gas and the adsorbent. A similar procedure may be followed for a chemical reaction whose rate equation and thermochemistry are known.

The evaluation of the complete distributions of temperature, reactants, and products as functions of time and position is a straightforward but tedious operation following the patterns previously described. In this operation the increments of time and distance used in establishing temperature variations must be related to the time and distance increments used in establishing variations in composition. For simplification the increments of u and v should be related as follows:

$$\Delta u' = \frac{a'}{a}\Delta u = \frac{H_d}{H_h}\Delta u \tag{105}$$

and

$$\Delta v' = \frac{b'}{b}\Delta v = \frac{C_G}{C_S}\frac{H_d}{H_h}\Delta v \tag{106}$$

PROBLEMS

1. It is desired to design a plant for the production of 15,000 lb per day of mononitrotoluene from toluene. A design study is to be made on the basis of a fresh mixed acid of the following composition in mole per cent:

HNO_3	45
H_2SO_4	30
H_2O	25
	100

It is desired to produce a conversion of 99.0 per cent with an excess of 3 per cent HNO_3 above that theoretically required.

(*a*) Using the data of Illustration 1, calculate the minimum reactor volume required in a batch operation at 30°C in which 2 hr are required for charging and emptying the reactor.

(*b*) Calculate the reactor volume required for a single-stage continuous operation under the conditions of part (*a*).

(*c*) Calculate the volumes of the reactor required for a two-stage counterflow operation in which 50 per cent of the total conversion is produced in each reactor. Neglect the formation of di- and trinitro compounds.

(*d*) Calculate the reactor volume required if the process is carried out in a two-stage counterflow operation with reactors of equal size.

2. For the reaction represented by Equation (17) derive rate equations corresponding to the following mechanisms:

(*a*) Reaction between an adsorbed *B* molecule and an adjacent active center with the rate of desorption of product *R* as the rate-determining step.

(*b*) Reaction on a single active center between gaseous *B* and solid *A* to form a chemisorbed *R* molecule and a gaseous *S* molecule. The rate-controlling step is the surface reaction.

3. Using the data and assumptions of Illustration 2, develop curves similar to those of Fig. 213 for combustion of the coke with an air rate of 150 lb/(sq ft) (hr) at an average temperature of 2400°F. Compare these results with Fig. 213.

4. Hard water is softened at a rate of 20 gal per min in an exchanger bed 2 sq ft in area and 2 ft thick. The initial hardness of the water is equivalent to 200 parts of calcium carbonate per million parts of water. The exchanger has an initial replaceable sodium content equivalent to 28,000 grains of calcium carbonate per cu ft. The density of the mineral is 30 lb per cu ft, grain size 20–28 mesh, and with a value of k_1 equal to 2.29.

(*a*) Calculate with and without use of Fig. 214, the residual hardness of the water after 5 hr of steady flow.

(*b*) Plot the residual hardness of water against time for a period of 24 hr by use of Fig. 214.

(*c*) Calculate with and without the use of Fig. 215 the time required to reach a residual hardness of seven parts per million and the gallons of water softened.

5. In a cation exchanger water is softened at the rate of 3 gal per sq ft per min in a bed 4 ft thick, having a density of 30 lb per cu ft and an exchange capacity of 20,000 grains of calcium carbonate per cu ft. The water has an initial hardness of 200 parts equivalent calcium carbonate per million. After operation for 8 hr, the water leaving has a residual hardness of 12.8 parts per million of calcium carbonate.

(*a*) Calculate the value of the reaction velocity constant k_1 as defined by Equation (32).

(*b*) Plot the residual hardness against time over a period of 16 hr.

6. Air at 70°F and 90 per cent relative humidity is passed isothermally through a bed of 2–4 mesh activated alumina 2 ft in thickness at a velocity of 50 ft per min (based upon total cross section of bed).

The bed is initially free of moisture. An average value of the adsorption equilibrium ratio m over the entire relative humidity range is 0.20.* The following properties of the bed are assumed: $\rho_B = 50$ lb per cu ft, $D_p = 0.0216$ ft, $a_v = 181$ sq ft per cu ft, 50 per cent external void space. Calculate, over a drying period of 4 hr and at the end of 1, 2 and 4 hr,

(*a*) The humidity of the air leaving the bed.
(*b*) The average humidity of the air leaving the bed.
(*c*) The moisture content gradient in the bed.
(*d*) The average moisture content of the bed.
(*e*) The total water adsorbed by a bed 10 sq ft in area.

7. Air at 80°F and 80 per cent relative humidity is passed through a bed of silica gel 6.8 mesh, 12 in. thick, at an entering rate of 136 ft per min based on total cross section. The drying of the air takes place isothermally. The bulk density of the gel is 39 lb per cu ft, and the value of m is 0.55.* At the end of 1 hr the relative humidity of the air leaving is 10 per cent. Calculate the value of $H_d a_v$ for the bed.

8. Benzene vapor present to the extent of 1.0 per cent by volume in hydrogen is to be removed by passing the gas mixture downward through a bed of silica gel at 80°F and 2 atm pressure at a linear velocity of 200 ft per min (based on total cross section). It is desired to operate for a period of 90 min with a minimum benzene recovery from the gas of 90 per cent. The silica gel is 2–4 mesh, with a bulk density of 39 lb per cu ft, and with the following estimated properties, $D_p = 0.0220$ ft, $a_v = 117$ sq ft per cu ft. The adsorption-equilibrium factor m for benzene on silica gel is 1.67.* Over the 1.5 hr period calculate:

(*a*) The depth of bed required.
(*b*) The concentration gradient of benzene in the bed.
(*c*) The total benzene removed by a bed 8 sq ft in area.

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* In problems 6, 7, and 8, m is defined by the relation $w = mp^*/p_s$ as used in Equation (65).

APPENDIX

ATOMIC WEIGHTS OF THE MORE COMMON ELEMENTS

Aluminum	Al	26.97	Manganese	Mn	54.93
Antimony	Sb	121.76	Mercury	Hg	200.61
Argon	A	39.944	Molybdenum	Mo	95.95
Arsenic	As	74.91	Neon	Ne	20.183
Barium	Ba	137.36	Nickel	Ni	58.69
Bismuth	Bi	209.00	Nitrogen	N	14.008
Boron	B	10.82	Oxygen	O	16.000
Bromine	Br	79.916	Phosphorus	P	30.98
Cadmium	Cd	112.41	Platinum	Pt	195.23
Calcium	Ca	40.08	Potassium	K	39.096
Carbon	C	12.010	Selenium	Se	78.96
Chlorine	Cl	35.457	Silicon	Si	28.06
Chromium	Cr	52.01	Silver	Ag	107.880
Cobalt	Co	58.94	Sodium	Na	22.997
Copper	Cu	63.57	Strontium	Sr	87.63
Fluorine	F	19.00	Sulfur	S	32.06
Gold	Au	197.2	Tellurium	Te	127.61
Helium	He	4.003	Tin	Sn	118.70
Hydrogen	H	1.008	Titanium	Ti	47.90
Iodine	I	126.92	Tungsten	W	183.92
Iron	Fe	55.85	Uranium	U	238.07
Lead	Pb	207.21	Vanadium	V	50.95
Lithium	Li	6.940	Zinc	Zn	65.38
Magnesium	Mg	24.32	Zirconium	Zr	91.22

Source: *J. Am. Chem. Soc.*, **63**, 850 (1941).

CONVERSION FACTORS AND CONSTANTS

Analysis of Air

By weight: oxygen, 23.2%; nitrogen, 76.8%
By volume: oxygen, 21.0%; nitrogen, 79.0%

Average molecular weight of air	29
Average molecular weight of atmospheric nitrogen	28.2

Physical Constants

The Gas Law Constant R

R = 1.987 (calories)/(g-mole)(°K)
R = 82.06 (cu cm)(atm)/(g-mole)(°K)
R = 10.71 (lb/sq in.)(cu ft)/(lb-mole)(°R)
R = 0.7302 (atm)(cu ft)/(lb-mole)(°R)

1 faraday = 96,500 coulombs
Avogadro constant = 6.023×10^{23} per gram-atom

Density

1 gram-mole of an ideal gas at 0°C, 760 mm of mercury = 22.414 liters
1 pound-mole of an ideal gas at 0°C, 760 mm of mercury = 359.0 cubic feet

Density of dry air at 0°C, 760 mm of mercury = 1.293 grams per liter or	0.0807 pound per cubic foot
1 gram per cc	62.4 pounds per cubic foot
1 gram per cc	8.337 pounds per U. S. gallon

Energy*

	Calories	Btu	Joules	Foot-pounds	Kilogram-meters
Calorie	1	3.968×10^{-3}	4.185	3.087	0.4267
Btu	252	1	1055	777.9	107.5
Joule	0.2389	9.482×10^{-4}	1	0.73756	0.1019
Foot-pound	0.3240	1.286×10^{-3}	1.356	1	0.13826
Kilogram-meter	2.343	9.298×10^{-3}	9.806	7.2327	1
Liter-atmos	24.21	9.607×10^{-2}	101.32	74.733	10.333
1 Chu	453.6	1.8	1899	1400	193.5

	Liter-atm	Cu ft-atm	Foot-poundals	Horsepower hours
Calorie	4.130×10^{-2}	1.459×10^{-3}	99.31	1.5591×10^{-6}
Btu	10.41	0.3676	25030	3.929×10^{-4}
Joule	9.869×10^{-3}	3.485×10^{-4}	23.73	3.725×10^{-7}
Foot-pound	1.3381×10^{-2}	4.7253×10^{-4}	32.174	5.0505×10^{-7}
Kilogram-meter	9.678×10^{-2}	3.4177×10^{-3}	232.7	3.6529×10^{-6}
Liter-atmos	1	3.5319×10^{-2}	2403.8	3.7734×10^{-5}
1 Chu	13.74	0.6617	45054	7.072×10^{-4}

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* From Perkins, *Introduction to General Thermodynamics*, John Wiley & Sons, Inc., Publishers, with permission.

Length

1 inch	2.540 centimeters
1 micron	10^{-6} meter
1 Ångström unit	10^{-10} meter

Mass

1 pound*	16 ounces*
1 pound*	7000 grains
1 pound*	453.6 grams
1 ton (short)	2000 pounds*
1 gram	15.43 grains
1 kilogram	2.205 pounds*

* Avoirdupois.

Mathematical Constants

e	2.7183
π	3.1416
$\ln N$	$2.303 \log N$

Power

1 kilowatt	56.92 British thermal units per minute
1 kilowatt	1.341 horsepower
1 horsepower	550 foot-pounds per second
1 watt	44.24 foot-pounds per minute
1 watt	14.34 calories per minute

Pressure

1 pound per square inch	2.04 inches of mercury
1 pound per square inch	2.31 feet of water
1 atmosphere	14.7 pounds per square inch
1 atmosphere	760 mm of mercury
1 atmosphere	29.92 inches of mercury

Temperature Scales

Degrees F	1.8 (degrees C) + 32
Degrees K	degrees C + 273.15
Degrees R	degrees F + 459.7

Volume

1 cubic inch	16.39 cubic centimeters
1 liter	61.02 cubic inches
1 cubic foot	28.32 liters
1 cubic meter	1.308 cubic yards
1 cubic meter	1000 liters
1 U. S. gallon	4 quarts
1 U. S. gallon	3.785 liters
1 U. S. gallon	231 cubic inches
1 British gallon	1.20094 U. S. gallons
1 cubic foot	7.481 gallons
1 liter	1.057 quarts
1 U. S. fluid ounce	29.57 cubic centimeters

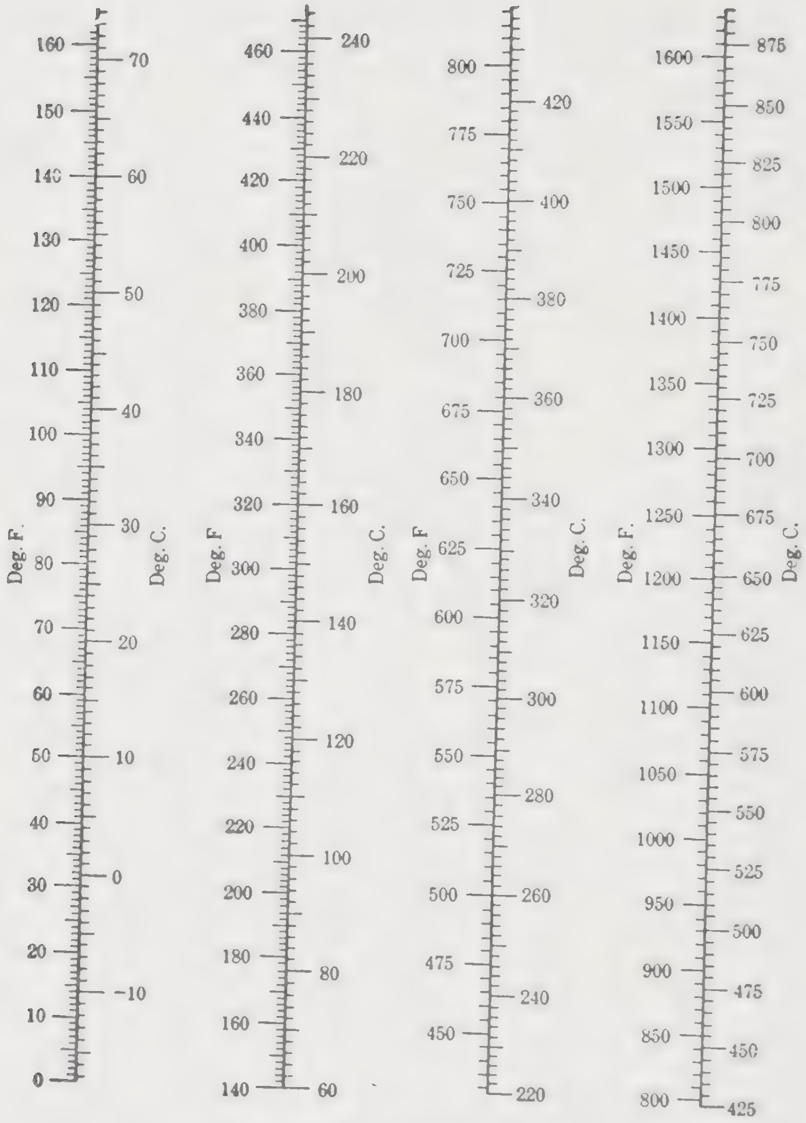

FIG. A. Temperature conversions.

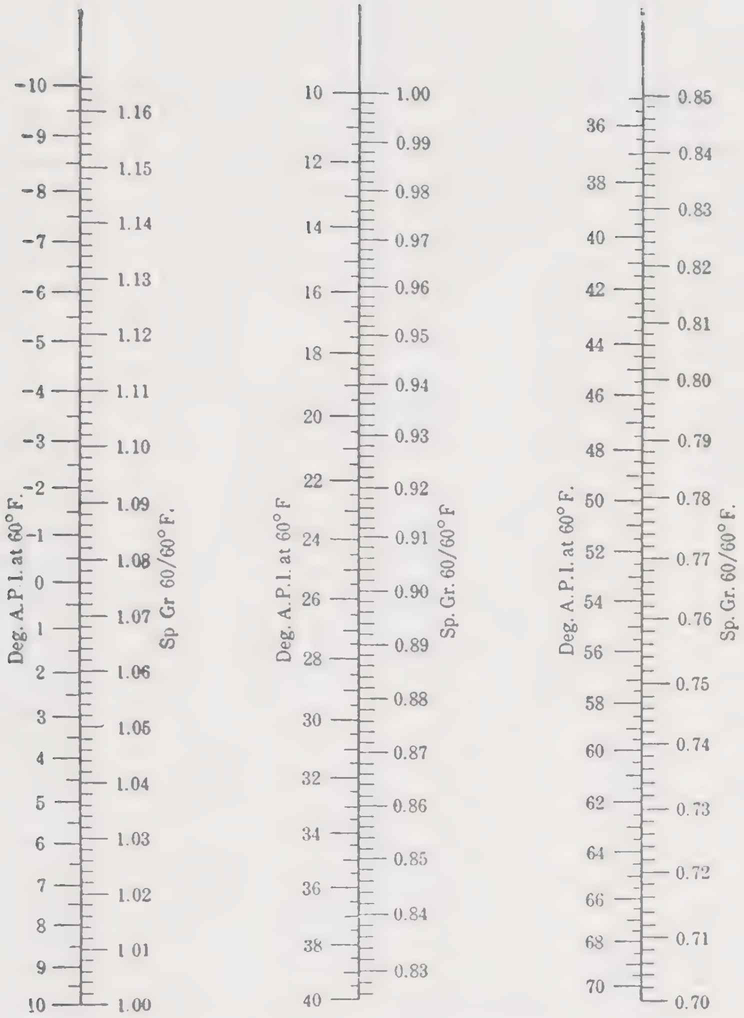

Fig. B. Gravity conversions.

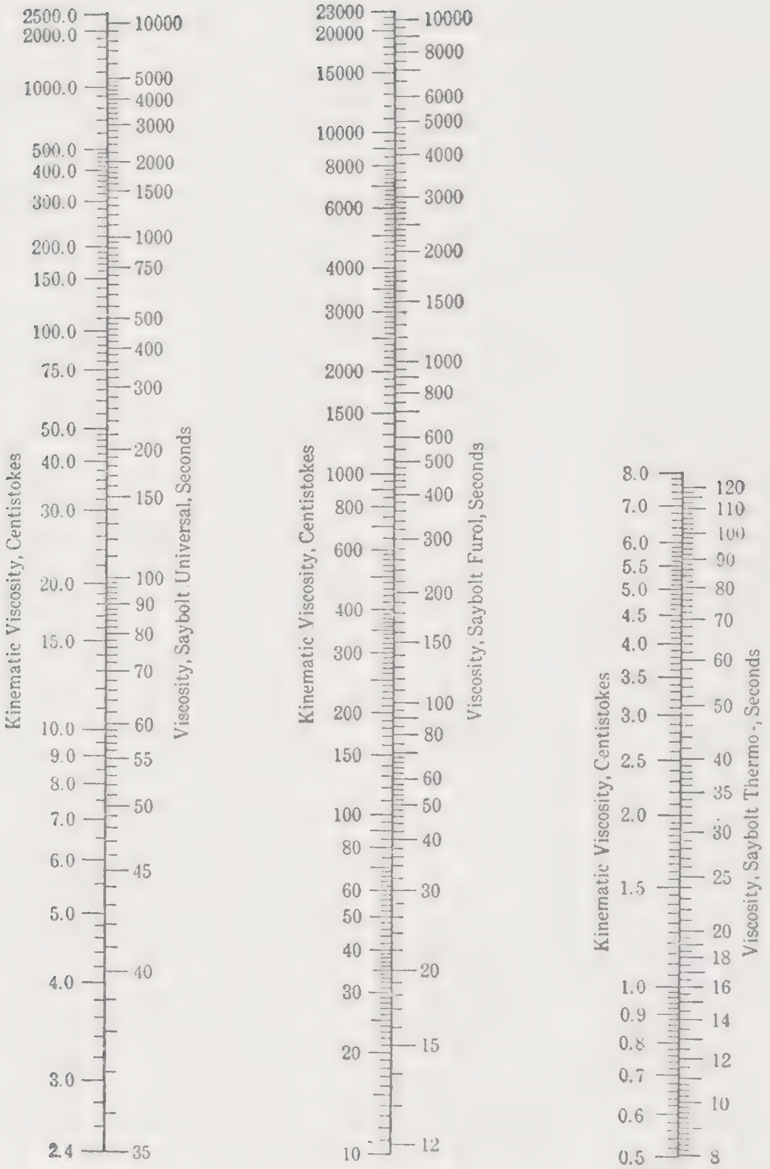

Fig. C. Viscosity conversions.

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